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<p>(54) Title: METHOD FOR PREPARING FLY ASH FOR HIGH COMPRESSIVE STRENGTH CONCRETE AND MORTAR, AND COMPOSITIONS THEREOF (57) Abstract  The present invention relates to concrete, mortar and other hardenable mixtures comprising cement and fly ash for use in construction. The invention relates to hardenable mixtures comprising cement and fly ash which can achieve greater compressive strength than hardenable mixtures containing only concrete over the time period relevant for construction. In a specific example, processing fly ash by grinding to the desired size distribution range gives a 100% yield of fly ash for utilization in high quality concrete and mortar. Such materials can thus significantly reduce construction costs, as well as provide a useful outlet for material that is generally regarded as a pollutant and a nuisance.</p>		

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**METHOD FOR PREPARING FLY ASH FOR HIGH COMPRESSIVE  
STRENGTH CONCRETE AND MORTAR,  
AND COMPOSITIONS THEREOF**

5

**FIELD OF THE INVENTION**

The present invention relates to concrete, mortar and other hardenable mixtures comprising cement and fly ash for use in construction. The invention includes a method for predicting the compressive strength of such a hardenable mixture, which is very  
10 important for planning a project. The invention also relates to hardenable mixtures comprising cement and fly ash which can achieve greater compressive strength than hardenable mixtures containing only cement without fly ash over the time period relevant for construction.

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**BACKGROUND OF THE INVENTION**

Fly ash, a by-product of coal burning power plant, is produced worldwide in large quantities each year. In 1988, approximately 84 million tons of coal ash were produced in the U.S. in the form of fly ash (60.7%), bottom ash (16.7%), boiler slag (5.9%), and flue  
20 gas desulfurization (16.7%) (Tyson, 1990, Coal Combustion By-Product Utilization Seminar, Pittsburgh, 15 pp.). Out of the approximately 50 million tons of fly ash generated annually, only about 10 percent is used in concrete (ACI Committee 226, 1987, "Use of Fly Ash In Concrete," ACI 226.3R-87, ACI J. Proceedings 84:381-409) while the remaining portion is mostly disposed of as waste in landfills.

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It is generally more beneficial for a utility to sell its ash, even at low or subsidized prices, rather than to dispose of it in a landfill, since this will avoid the disposal cost. In the 1960's and 70's the cost of ash disposal was typically less than \$1.00 per ton. However, due to the more stringent environmental regulations starting in the late 1970's, the cost of  
30 ash disposal has rapidly increased to from \$2.00 to \$5.00 per ton and is still rising higher (Bahor and Golden, 1984, Proceedings, 2nd International Conference on Ash Technology and Marketing, London, pp. 133-136). The shortage of landfill due to environmental concerns has further escalated the disposal cost. The Environmental Protection Agency (EPA) estimated in 1987 that the total cost of waste disposal at coal fired power plants  
35 ranged from \$11.00 to \$20.00 per ton for fly ash and bottom ash (Courst. 1991, Proceedings: 9th Int'l Ash Use Symposium, 1:21-1 to 21-10). This increasing trend of

disposal cost has caused many concerns and researchers are urgently seeking means for better utilization of fly ash. One potential outlet for fly ash is incorporation in concrete or mortar mixtures.

- 5 Fly ash is used in concrete in two distinct ways, one as a replacement for cement and the other as a filler. The first use takes advantage of the pozzolan properties of fly ash, which, when it reacts with lime or calcium hydroxide, can enhance the strength of cementitious composites. However, fly ash is relatively inert and the increase in compressive strength can take up to 90 days to materialize. Also, since fly ash is just a  
10 by-product from the power industry, the quality of fly ash has always been a major concern to the end users in the concrete industry.

Incorporation of fly ash in concrete improves workability and thereby reduces the water requirement with respect to the conventional concrete. This is most beneficial where  
15 concrete is pumped into place. Among numerous other beneficial effects are reduced bleeding, reduced segregation, reduced permeability, increased plasticity, lowered heat of hydration, and increased setting times (ACI Committee 226, 1987, *supra*). The slump is higher when fly ash is used (Ukita et al., 1989, SP-114, American Concrete Institute, Detroit, pp.219-240).

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However, the use of fly ash in concrete has many drawbacks. For example, addition of fly ash to concrete results in a product with low air entrainment and low early strength development.

- 25 As noted above, a critical drawback of the use of fly ash in concrete is that initially the fly ash significantly reduces the compressive strength of the concrete. Tests conducted by Ravindrarajah and Tam (1989, Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, SP-114, American Concrete Institute, Detroit, pp. 139-155) showed that the compressive strength of fly ash concrete at early ages are lower than those for the control  
30 concrete, which is a general property of concrete or mortar when fly ash is added. Most of the reported studies tend to show a lower concrete strength due to the presence of fly ash; none has yet suggested a solution to actually enhance the property of concrete economically. Yet, for fly ash to be used as a replacement for cement, it must be comparable to cement in terms of strength contribution at a point useful in construction.

As a practical matter, this means that the fly ash concrete must reach an acceptable compressive strength within about 2 weeks.

- Swamy (1984, Proceedings, 2nd Int'l Conference on Ash Technology and Marketing, London, pp. 359-367) showed that 30% replacement by weight, and inclusion of a high dose of a superplasticizer, yielded concrete with material properties and structural behavior almost identical to those of concrete of similar strength without fly ash. However, due to the high cost of superplasticizer, mix proportions were not economical.
- 10 Fly ashes from different sources may have different effect to concrete. The same fly ash may behave differently with Portland cements of different types (Popovics, 1982, ACI J. Proceedings 79:43-49), since different types of Portland cement (type I to V) have different chemical composition. Other factors relating to the effects of fly ash on concrete that are not presently understood are lime availability, the rate of solubility and reactivity
- 15 of the glassy phase in different fly ash, and the proper mix proportion to ensure early strength development of fly ash concrete.

- Fly ash particles are typically spherical, ranging in diameter from 1 to 150 microns (Berry and Malhotra, 1980, ACI J. Proceedings 77:59-73). Aitcin et al. (1986, Fly Ash, Silica
- 20 Fume, Slag, and Natural Pozzolans in Concrete, SP-91, American Concrete Institute, Detroit, pp. 91-113) showed that if the average diameters,  $D_m$ , of fly ash are smaller, the surface area of the fly ash will be larger than those with larger average diameters.

- Many factors affect the size or average diameter of fly ash, including storage conditions,
- 25 ash collection processes, and combustion conditions. Combustion conditions are perhaps most important, because these determine whether carbon remains in the ash or if combustion is complete.

- There are two main forms of combustion: dry bottom boiler combustion and wet bottom
- 30 boiler combustion. The main difference between the two types of boiler is that wet bottom boilers reach the fusion temperature of ash, thus resulting in fly ash with greater glass characteristics.

There are generally two methods known to measure the fineness of fly ash. The first is

by measuring the residue on the 45 micron (No. 325 sieve), which is the method used in the United States. The second method is the surface area method by air permeability test. Lane and Best (1982, Concrete Int'l: Design & Construction 4:81-92) suggested that 45 microns sieve residue is a consistent indicator of pozzolanic activity. For use in concrete or mortar, ASTM C 618 (1990, ASTM C 618-89a, *Annual Book of ASTM Standards*, Vol. 04.02) specifies that not more than 34% by weight of a given fly ash be retained on a 45 microns sieve. However, Ravina (1980, Cement and Concrete Research 10:573-580) reported that specific surface area provides a more accurate indicator of pozzolanic activity.

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Research carried out by Ukita et al. (1989, *supra*) purported that as the percentage of finer particles, *i.e.*, those particles ranging from diameters of 1 to 20 microns, in concrete increases, the corresponding strength gain is notable. Similar observations have been reported by Giergiczny and Werynska (1989, Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, SSP-114, American Concrete Institute, Detroit, pp. 97-115).

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Both of the groups mentioned above describe results with fly ash of disparate characteristics and sources, but did not include controls for these variable. Thus, although the emphasis of these reports is on the performance of finer particle fly ashes, the variables introduced into the studies lead to reservations with respect to any conclusions that may be drawn. In particular, Ukita et al. (1989, *supra*) collected fly ash from different locations. However, an earlier report demonstrated that fly ashes collected from different locations have different chemical properties (Liskowitz et al., 1983, "Sorbate Characteristic of Fly Ash," Final Report, U.S. Dept. of Energy, Morgantown Energy Technology Center, p. 211). Giergiczny and Werynska (1989, *supra*) ground the original fly ash into different sizes. Grinding can add metal particles into the fly ash, and also tends to yield unnaturally shaped particles of fly ash. Thus, these reports fail to provide conclusive information about the effect of fine particle size on the properties imparted by fly ash.

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Berry et al. (1989, Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, SP-114, American concrete Institute, Detroit, pp. 241-273) studied the properties of fly ash with particle size smaller than 45 microns, so called "beneficiated" fly ash, in mortar. Fly ashes of this particle size showed improved pozzolanic activity, reduced water demand and

enhanced ability to reduce alkali-aggregate reactivity.

Although beneficiated fly ash seem to show promising results in terms of improved performance of mortar, other researchers concluded otherwise when used in concrete.

- 5 Giaccio and Malhotra (1988, Cement, Concrete, and Aggregates 10:88-95) also conducted the test using the beneficiated fly ashes. They showed that the concrete made with ASTM type I cement, the use of beneficiated fly ash and condensed silica fume did little to enhance the properties of concrete compared with the raw fly ash.

- 10 There is a need in the art to utilize all of the fly ash produced in coal-dust fired boilers.

There is a further need to process fly ash efficiently to provide about 100% yield of useful product.

- 15 There is a further need in the art for high strength concrete and mortar containing fly ash.

There is yet a further need in the art for the utilization of fly ash generated during coal combustion.

- 20 These and other needs in the art are addressed in the instant application.

The citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

25 SUMMARY OF THE INVENTION

- The present invention relates to hardenable mixtures comprising processed fly ash of a defined fineness as a replacement for cement in cementitious materials, which hardenable mixtures achieve compressive strength that is about equal to or greater than the
- 30 compressive strength of the same hardenable mixture without fly ash in a time period that is acceptable for construction and other applications. In particular embodiments, the hardenable mixture can be concrete or mortar, as hereinafter defined.

The invention is related to the invention disclosed and claimed in U.S. Patent Application

No. 08/246,875, filed May 20, 1995, and in International Patent Publication No. WO 95/32423, published November 30, 1995, of PCT International Patent Application No. PCT/US95/06182, both entitled "IMPROVED COMPRESSIVE STRENGTH OF CONCRETE AND MORTAR CONTAINING FLY ASH". However, the present invention is based on the discovery that fly ash having desirable characteristics, such as a fineness modulus as defined in Application Serial No. 08/246,875 and International Publication No. WO 95/32423 (PCT/US95/06182), can be prepared by processing fly ash from boilers so as to shift the entire distribution of sizes to a desired range, while retaining substantially uniform spherical shape of the processed fly ash. This invention advantageously avoids the need for size fractionation, *e.g.*, by air classification, and provides a product with approximately 100% yield that, when incorporated in a hardenable mixture, such as concrete or mortar, demonstrates compressive strength properties that are equal to or better than fractionated fly ash achieves with such classification methodology, such as air classification.

An important advantage of the present invention relates to the improved compressive strength properties contributed by the processed fly ash hardenable mixtures. For example, in mortar prepared using processed fly ash of the invention to replace 25% of the cement, "cross-over" in compressive strength of the mortar compared with a control mortar occurs within 7 to 14 days, and the compressive strength of the mortar containing processed fly ash is 50% greater than the control after 56 days.

As noted above, another advantage of the invention is that the process does not require fractionation, and allows for utilization of about 100% of the fly ash obtained from a boiler operation. Quantitative utilization of the fly ash avoids the need to dispose of undesirable fly ash fractions, which addressed the concerns of utilities for abatement of this otherwise undesirable pollutant.

A further advantage of the invention is that the grinding process appears to release ammonia captured in the surface of fly ash produced from urea-treated coal (which is used to reduce NO<sub>x</sub> emissions). The presence of ammonia in fly ash renders it unsuitable for use in concrete or mortar.

Yet another advantage of the present invention is that processing minimizes the effects of



boiler conditions on fly ash properties associated with boiler conditions and the degree of coal pulverization. Accordingly, fly ash can be dry bottom boiler fly ash or wet bottom boiler fly ash.

- 5 The processed fly ash of the invention is characterized by having the following properties: substantially uniform spherical shape; greater than about 90% of the particles have a diameter of less than 11  $\mu\text{m}$ , greater than about 60% of the particles have a diameter of less than 5.5  $\mu\text{m}$ , and greater than about 15% of the particles have a diameter of less than 1.375  $\mu\text{m}$ ; a median particle diameter of less than about 4.0  $\mu\text{m}$ ; and a range of particle
- 10 diameters of from about 0.1  $\mu\text{m}$  to about 70  $\mu\text{m}$ . Preferably, greater than about 93% of the particles have a diameter of less than 11  $\mu\text{m}$ , greater than about 70% of the particles have a diameter of less than 5.5  $\mu\text{m}$ , and greater than about 18% of the particles have a diameter of less than 1.375  $\mu\text{m}$ . In another preferred aspect, the median particle diameter is less than about 3.0  $\mu\text{m}$ . In yet another preferred aspect, the range of particle diameters
- 15 is from about 0.9  $\mu\text{m}$  to about 62  $\mu\text{m}$ . In a specific embodiment, the fly ash is prepared by grinding unfractionated fly ash.

- As shown in a specific example, *infra*, the preferred characteristics of the fly ash are as follows: greater than about 93% of the particles have a diameter of less than 11  $\mu\text{m}$ ,
- 20 greater than about 70% of the particles have a diameter of less than 5.5  $\mu\text{m}$ , and greater than about 18% of the particles have a diameter of less than 1.375  $\mu\text{m}$ ; the median particle diameter is less than about 3.0  $\mu\text{m}$ ; and the range of particle diameters is from about 0.9  $\mu\text{m}$  to about 62  $\mu\text{m}$ .
- 25 In another aspect, the invention is directed to fly ash prepared by processing fly ash so as to shift the size distribution to have the characteristics noted above, *i.e.*, substantially uniform spherical shape; greater than about 90% of the particles have a diameter of less than 11  $\mu\text{m}$ , greater than about 60% of the particles have a diameter of less than 5.5  $\mu\text{m}$ , and greater than about 15% of the particles have a diameter of less than
- 30 1.375  $\mu\text{m}$ ; a median particle diameter of less than about 4.0  $\mu\text{m}$ ; and a range of particle diameters of from about 0.1  $\mu\text{m}$  to about 70  $\mu\text{m}$ . In a specific example, *infra*, the processing comprises grinding with a fluid bed grinding process with a low ratio of fly ash to grinding media. In a specific embodiment, *infra*, about two parts unfractionated fly ash are ground with about one part grinding media (by volume), and the grinding media is

zirconium silicate. However, other grinding media, such as carbon steel, are also contemplated for use according to the invention.

Naturally, in addition to fly ash, the present invention is directed to a method for  
5 preparing fly ash comprising processing fly ash so as to shift the size distribution to have the desired characteristics as set forth above. In a preferred embodiment, exemplified *infra*, the method of processing comprises grinding with a fluid bed grinding process with a low ratio of fly ash to grinding media. In a specific example, about two parts of unfractionated fly ash are processed with about one part grinding media (by volume). In a  
10 specific embodiment, the grinding media is zirconium silicate. In another embodiment, the grinding media may be carbon steel.

As is readily apparent to one of ordinary skill in the art, selection of starting material and grinding conditions are necessary to yield the fly ash of the invention. In a specific  
15 embodiment exemplified herein, unfractionated (unclassified) fly ash unexpectedly yields a superior processed fly ash product after grinding; a coarse fraction of fly ash does not yield the same quality processed fly ash product under the same grinding conditions.

As noted above, the present invention is directed to hardenable mixtures comprising fly  
20 ash processed according to the invention. For example, the invention is directed to concrete comprising about 1 part by weight cementitious materials, about 1 to about 3 parts by weight fine aggregate, about 1 to about 5 parts by weight coarse aggregate, and about 0.35 to about 0.6 parts by weight water, wherein the cementitious materials comprise from about 10% to about 50% by weight the fly ash of the invention and about  
25 50% to about 90% by weight cement. Concrete of the invention may further comprise silica fume or glass fibers.

In another embodiment, the hardenable mixture is a mortar comprising about 1 part by weight cementitious materials, about 1 to about 3 parts by weight fine aggregate, and  
30 about 0.35 to about 0.6 parts by weight water, wherein the cementitious materials comprise from about 10% to about 50% by weight the fly ash of the invention and about 50% to about 90% by weight cement. Mortar of the invention may further comprise silica fume or glass fibers.

In a further aspect, in a hardenable mixture, *i.e.*, concrete or mortar, of the invention, the fine aggregate may comprise sand and fly ash, wherein a ratio by weight of sand to fly ash is from about 4:1 to about 1:1. Preferably, the fly ash has a fineness modulus of less than about 600, wherein the fineness modulus is calculated as the sum of the percent of fly ash retained on sieves of 0, 1, 1.5, 2, 3, 5, 10, 20, 45, 75, 150, and 300 microns (as described in Application Serial No. 08/246,875 and International Publication No. WO 95/32423). In another embodiment, the fly ash used as fine aggregate is processed fly ash of the invention.

#### 10 **BRIEF DESCRIPTION OF THE DRAWINGS**

**FIGURE 1.** Compressive strength of fly ash mortar prepared with the M8F95 air classified product, used to replace 25% of cement. Three series of mortars were prepared (square, lozenge, and triangle).

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**FIGURE 2.** Compressive strength of fly ash mortar prepared with the M9F95 air classified product, used to replace 25% of cement. Three series of mortars were prepared (square, lozenge, and triangle).

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**FIGURE 3.** Compressive strength of fly ash mortar prepared with the M8F95 air classified product, used to replace 35% of cement. Three series of mortars were prepared (square, lozenge, and triangle).

25 **FIGURE 4.** Compressive strength of fly ash mortar prepared with the M9F95 air classified product, used to replace 35% of cement. Three series of mortars were prepared (square, lozenge, and triangle).

**FIGURE 5.** Compressive strength of fly ash mortar prepared with the M13N94 air  
30 classified product, used to replace 25% of cement. Three series of mortars were prepared (square, lozenge, and triangle).

**FIGURE 6 (prior art).** Schematic diagram of the dry grinding process employed to process the coarse fraction of air classified fly ash, and unfractionated fly ash. The

Attritor dry grinding process is achieved in a stationary tank by means of a rotating shaft and arms that agitate the media into a random state of motion of internal porosity called kinematic porosity. In this expanded condition, the media and particles are free to move, collide, and impinge upon each other. (A) Kinematic porosity in expanded media. The revolving arm hits grinding media. The media moves forward rapidly. The media collides with the substrate, breaking up or reducing in size the product particle. (B) Media at rest when the shaft is stationary. (C) Expanded media when the shaft is rotating.

10 **FIGURE 7.** Analysis of the particle size distribution and mode for the coarse air classified fly ash fraction (M8C95) prior to grinding.

**FIGURE 8.** Analysis of the particle size distribution and mode for the unfractionated fly ash (M0C95) prior to grinding.

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**FIGURE 9.** Compressive strength of fly ash mortar prepared with the M0G95 (ground, unfractionated fly ash) product, used to replace 25% of cement. Three series of mortars were prepared (square, lozenge, and triangle).

20 **FIGURE 10.** Compressive strength of fly ash mortar prepared with the M8CG95 air classified product after grinding, used to replace 25% of cement. Three series of mortars were prepared (square, lozenge, and triangle).

**FIGURE 11.** Compressive strength of fly ash mortar prepared with the M0G95 product, after grinding, used to replace 35% of cement. Three series of mortars were prepared (square, lozenge, and triangle).

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**FIGURE 12.** Compressive strength of control fly ash mortar prepared with cement without fly ash. Three series of mortars were prepared (square, lozenge, and triangle).

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#### DETAILED DESCRIPTION OF THE INVENTION

As described above, the present invention relates to hardenable mixtures comprising processed fly ash of a defined fineness as a replacement for cement in cementitious

materials, which hardenable mixtures achieve compressive strength that is about equal to or greater than the compressive strength of the same hardenable mixture without fly ash. The invention further provides for replacement of a portion of the fine aggregates in a hardenable mixture with fly ash of a defined fineness. In particular embodiments, the  
5 hardenable mixture can be concrete or mortar, as hereinafter defined.

Throughout this specification, where specific ratios, percentages, or proportions are mentioned, they are determined by weight and not by volume unless stated otherwise.

10 The present invention is based, in part, on the observation that processing fly ash from a boiler to shift the entire distribution range of fly ash particles to a smaller size, and to narrow that range, allows for essentially quantitative utilization of fly ash, and yields hardenable mixtures, *e.g.*, concrete and mortar, with a greater rate of compressive strength gain than other such compositions comprising fly ash, and crossover for greater  
15 compressive strength than such mixtures lacking fly ash after seven to fourteen days. These properties are independent of the source and chemical composition of fly ash, as the pozzolanic properties of the fly ash primarily depend on the degree of fineness of the fly ash. It has been surprisingly found that processing fly ash by grinding to a defined fineness modulus as herein defined provides a high degree of quality control, regardless of  
20 the classification or combustion conditions of the fly ash.

As used herein, the term "fly ash" refers to a solid material having a chemical composition similar to or the same as the composition of the material that is produced during the combustion of powdered coal. In a specific aspect, the solid material is the  
25 material remaining after the combustion of powdered coal. ACI Committee 116 (1990, ACI 116-85, *ACI Manual of Concrete Practice Part I*, American Concrete Institute, Detroit) defines fly ash as "the finely divided residue resulting from the combustion of ground or powder coal which is transported from the firebox through the flue gases", and the term "fly ash" as used herein encompasses this definition. Generally, fly ash derived  
30 from various coals have differences in chemical composition, but the principal components of fly ash are  $\text{SiO}_2$  (25% to 60%),  $\text{Al}_2\text{O}_3$  (10% to 30%), and  $\text{Fe}_2\text{O}_3$  (5% to 25%). The MgO content of fly ash is generally not greater than 5%. Thus, the term fly ash generally refers to solid powders comprising from about 25% to about 60% silica, from about 10% to about 30%  $\text{Al}_2\text{O}_3$ , from about 5% to about 25%  $\text{Fe}_2\text{O}_3$ , from about 0% to about 20%

CaO, and from about 0% to about 5% MgO.

The term "fly ash" further contemplates synthetic fly ash, which may be prepared to have the same performance characteristics as fly ash as described herein.

5

Presently, fly ash is classified primarily in two groups: Class C and Class F, according to the ASTM C 618 (1990, *supra*). Class F is generally produced by burning bituminous coal, and Class C results from sub-bituminous coal or lignite. Generally, the fly ash from the combustion of sub-bituminous coals contains more CaO and less  $\text{Fe}_2\text{O}_3$  than fly ash from bituminous coal (Berry and Malhotra, 1980, ACI J. Proceedings 77:59-73). Thus, the CaO content of the Class C fly ash is usually higher than 10%, with the sum of the oxides of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  not less than 50%. For Class F fly ash the CaO content is normally less than 10% and the sum of the above mentioned oxides is not less than 70%.

15

The glassy phase of fly ash depends essentially on the combustion conditions and type of boiler. Non-fractionated fly ash obtained from different boilers, such as dry bottom boilers or wet bottom boilers, has been found to behave differently. Boilers that achieve higher temperature yield fly ash with a more developed or pronounced glassy phase. Alternatively, combustion in the presence of a fluxing agent, which reduces the fusion temperature of the fly ash, can also increase the glassy phase of fly ash produced by combustion for lower temperature boilers. Compressive strength of a hardenable mixture containing fly ash may depend in part on the glassy phase of the fly ash, so generally fly ash produced for higher temperature boilers, or produced in the presence of a fluxing agent, or both, may be preferred. However, the fineness modulus is the most important parameter for defining compressive strength, and fractionated fly ash from any source, with a defined fineness modulus, can be used according to the invention.

Although fly ash generally comes in a dry and finely divided form, in many instances, due to weathering and transportation processes, fly ash becomes wet and often forms lumps. Such fly ash can be less reactive.

Pozzolan, as defined by ASTM C 593 (1990, ASTM C 593-89, *Annual Book of ASTM Standards*, Vol. 04.02), is "a siliceous or aluminosiliceous material that in itself possesses

little or no cementitious value but that in finely divided form and in the presence of moisture will chemically react with alkali and alkaline earth hydroxides at ordinary temperatures to form or assist in forming compounds possessing cementitious properties."

- 5 The present invention relates to the determination of the fineness modulus of fractionated fly ash. As used herein, the term "fineness modulus" refers to a measure of the distribution of volumes of particles of fly ash or distribution of particle sizes of the fly ash. According to the present invention, the fineness modulus is a distribution analysis that is much more informative than an average or median particle diameter determination
- 10 or total surface area determination. The value of fineness modulus corresponds to the fineness of a fraction of fly ash, or to non-fractionated fly ash. Thus, a fraction of fly ash containing a distribution of particles having smaller size, *e.g.*, a median diameter that falls within a smaller range set, will have a fineness modulus value that is lower than a fraction of fly ash containing a distribution of particles having somewhat larger size, *e.g.*, a
- 15 median diameter that falls within a larger range set, or non-fractionated fly ash. According to the present invention, lower values of fineness modulus are preferred, since hardenable mixtures that contain fractions having a lower fineness modulus achieve compressive strength gains more rapidly. In another embodiment, larger values of fineness modulus may be preferred, where a slower rate of compressive strength gain may
- 20 be desired.

The fineness modulus can be determined experimentally, *e.g.*, by sequentially sieving fly ash particles on different sized sieves, or by light diffraction index analysis. The latter method provides a basis for virtual sieving by indicating the size distribution and number,

25 thus allowing for prediction of percent retention (or pass through) on a sieve of a given size.

Thus, the present invention is directed, in part, to use of processed fly ash, in which the fly ash particles in any given fraction have a more uniform distribution of volumes, sizes,

30 and regular spherical shape than non-fractionated fly ash, or fly ash processed by crushing or other techniques that fracture the particles, resulting in irregular, microscopically jagged shape.

Preferably, the fineness modulus is determined as the sum of the percentage of fly ash

remaining on each of a series of different sized sieves. As noted above, this value can be a virtual number, determined by predicting the percent retention on different sized sieves from size information derived using other techniques. Accordingly, the term "fineness modulus" refers to a relative value, which can vary depending on the series of sieves (or other sizing apparatus) chosen. Since, according to the instant invention, fly ash particles of smaller size or diameter are preferred for use in hardenable mixtures, more accurate determinations of fineness modulus are available if a series of smaller sieves are chosen. Preferably, the size of the sieves is predominantly below 10  $\mu$ , *e.g.*, the sieves may be 0.5, 1, 2, 3, 4, 5, 6, 7, 8 and 10 microns, with sieves ranging up to 300 microns being useful. The number of sieves sized 10 microns or less should be at least one more than the number of sieves sized greater than 10 microns. In a preferred embodiment, the number of sieves sized 10 microns or less is at least five. Although in a specific embodiment dry sieves are used to calculate a value for the fineness modulus, other methods, such as wet sieving, can also be used. Quantitative determination of fineness modulus, as well as preparation of hardenable mixtures with greater rates of increase in compressive strength, is more fully developed in co-pending U.S. Patent Application Serial No. 08/246,875, filed May 20, 1994 by Liskowitz et al., entitled "IMPROVED COMPRESSIVE STRENGTH OF CONCRETE AND MORTAR CONTAINING FLY ASH," and International Patent Publication No. WO 95/32423, published November 30, 1995, of International Patent Application No. PCT/US95/06182, filed May 19, 1995, by Liskowitz et al. and having the same title.

The greater the number of sieves sized 10 microns or less, the greater the absolute value of fineness modulus. Accordingly, where sieves of 0.5, 1, 2, 3, 4, 5, 6, 7, 8, and 10 microns are used, the fineness modulus will be a higher absolute number, reflective of the greater degree of accuracy of determination of this value for the smaller diameter or smaller size fly ash particles.

Although not intending to be bound by any particular theory or hypothesis, it is believed that dissolution of fly ash in a hardenable mixture, whereby the pozzolanic properties of the fly ash can contribute to compressive strength of the hardenable mixture, is acutely dependent on the size distribution of the fly ash to a certain minimum size. It has been further discovered that fly ash particles with a uniform, generally spherical, shape are preferred because they do not degrade the workability of cementitious mixtures. The data



disclosed in the Examples, *infra*, support a conclusion that the fly ash contribution to compressive strength of a hardenable mixture depends on the distribution of particle volumes, or sizes. Above a minimum size, the contribution diminishes. Below this minimum size, strength of the concrete appears to be independent of size. Most surprising  
5 is the discovery that a regular, predominantly spherical, surface is preferred. This observation is surprising because the surface area hypothetically determines the reactivity of a particle, since surface functional groups are presumably more available for reaction, and thus one might expect that an irregular surface area, such as with a jagged particle, would be preferred.

10

The pozzolanic reaction of fly ash in a hardenable mixture comprising cement is the reaction between constituents of the fly ash and calcium hydroxide or other alkaline materials. It is generally assumed to take place on the surface of fly ash particles, between silicates and aluminates from the glass phase of the fly ash and hydroxide ion in  
15 the pore solution (Plowman, 1984, Proceedings, 2nd Int'l Conference on Ash Technology and Marketing, London, pp. 437-443). However, the result of the research leading to the present invention indicates that the pozzolanic reactions of the ash are dependent on the volume and shape of the fly ash particles: the smaller the particle volume, and the more regular its shape, the more rapidly it completes its reaction with the cement to contribute  
20 to compressive strength. The rate of solubility and reactivity of these glassy phases in different types of fly ash depends on the glassy phase of fly ash, which in turn depends on the combustion temperature of the boiler that produced the fly ash. In addition to the effect of combustion conditions on the glassy phase of fly ash, different fly ashes from one class can behave differently, depending on the  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  content, and other  
25 factors such as the particle size distribution and storage conditions of the ash (*see* Aitcin et al, 1986, *supra*; Liskowitz et al., 1983, *supra*).

During hydration, Portland cement produces a surfeit of lime ( $\text{CaO}$ ) that is released to the pore spaces. It is the presence of this lime that allows the reaction between the silica  
30 components in fly ash and calcium hydroxide to form additional calcium silicate hydrate [C-S-H]. He et al. (1984, Cement and Concrete Research 14:505-511) showed that the content of crystalline calcium hydroxide in the fly ash-Portland cement pastes decreases as a result of the addition of fly ash, most likely resulting from a reaction of calcium with alumina and silica from fly ash to form additional C-S-H. This process stabilizes the

concrete, reduces permeability and increases resistance to chemical attacks.

Processing of fly ash to achieve the desired fineness modulus, *i.e.*, distribution of sizes, can be accomplished by any means known in the art, provided that it preserves or results in particles of fairly regular, preferably spherical, shape. Preferably, processing comprises grinding with a fluid bed grinding process with a low ratio of fly ash to grinding media. In a specific embodiment, *infra*, about two parts unfractionated fly ash are ground with about one part grinding media (by volume), and the grinding media is zirconium silicate. However, other grinding media, such as carbon steel, are also contemplated for use according to the invention.

The term "cement" as used herein refers to a powder comprising alumina, silica, lime, iron oxide and magnesia burned together in a kiln and finely pulverized, which upon mixing with water binds or unites other materials present in the mixture in a hard mixture. Thus, the hardenable mixtures of the invention comprise cement. Generally, the term cement refers to hydraulic cements such as, but not limited to, Portland cement, in particular Portland type I, II, III, IV and V cements.

As used herein, the term "cementitious materials" refers to the portion of a hardenable mixture that provides for binding or uniting the other materials present in the mixture, and thus includes cement and pozzolanic fly ash. Fly ash can comprise from about 5% to about 50% of the cementitious materials in a hardenable mixture of the invention; preferably, fly ash comprises from about 10% to about 35% of cementitious materials. The balance of cementitious materials will generally be cement, in particular Portland cement. In a specific embodiment, *infra*, the hardenable mixtures of the invention comprise Portland type I cement.

The term "concrete" refers to a hardenable mixture comprising cementitious materials; a fine aggregate, such as sand; a coarse aggregate, such as but not limited to crushed basalt coarse aggregate; and water. Concrete of the invention further comprises fly ash having defined fineness. In a specific embodiment, the fly ash makes up from about 10% to about 50% of the cementitious materials. In a further aspect, the fly ash is used as fine aggregate in a ratio of from about 4:1 to about 1:1 to sand. In yet a further embodiment, the fly ash is an additive in addition to a replacement of cement, or a replacement of

cement and fine aggregate.

Various ratios of cement, fine aggregate, coarse aggregate, water, and optionally additives as set forth below, are used to prepare concrete, and are contemplated by the present invention. In specific embodiments, concrete of the invention consists essentially of about 1 part by weight cementitious materials, about 1 to about 3 parts by weight fine aggregate, about 1 to about 5 parts by weight coarse aggregate, about 0.35 to about 0.6 parts by weight water, and optionally additives as set forth below, such that the ratio of cementitious materials to water ranges from approximately 3:1 to 1.5:1; preferably, the ratio of cementitious materials to water is about 2:1. In a specific embodiment, the concrete consists essentially of 1 part cementitious materials, 2 parts siliceous river sand or Ottawa sand, 3 parts 3/8" crushed basalt coarse aggregate, and 0.5 parts water.

The term "mortar" refers to a hardenable mixture comprising cementitious materials; a fine aggregate, such as sand; and water. Mortar of the invention further comprises fly ash having defined fineness. In a specific embodiment, the fly ash makes up from about 10% to about 50% of the cementitious materials. In a further aspect, the fly ash is used as fine aggregate in a ratio of from about 4:1 to about 1:1 to sand. In yet a further embodiment, the fly ash is an additive in addition to a replacement of cement, or a replacement of cement and fine aggregate.

Various ratios of cement, fine aggregate, water, and optionally additives as set forth below, are used to prepare mortar, and are contemplated by the present invention. In specific embodiments, mortar of the invention consists essentially of about 1 part by weight cementitious materials, about 1 to about 3 parts by weight fine aggregate, about 0.5 parts by weight water, and optionally additives, such that the ratio of cementitious materials to water is approximately 2:1. In a specific embodiment, the mortar consists essentially of 1 part cementitious materials, 2.75 parts Ottawa sand, and 0.5 parts water.

As noted above, fly ash can be used as a fine aggregate in concrete or mortar, in addition to having a role as a cementitious material. It has been found that substituting fly ash for a conventional fine aggregate, such as sand, provides the advantages of increased compressive strength of the concrete or mortar since the total amount of fly ash in the hardenable composition is the same, with a rapid rate of increase of compressive strength

because the amount of cement in the cementitious materials is greater.

According to the present invention, the hardenable mixture can further comprise one or more of the following in quantities commonly used in concrete and mortar compositions:

- 5 kiln dust, *e.g.*, the dust generated in the manufacture of cement; silica fume, which is a by-product from the silicon metal industry usually consisting of about 96%-98% reactive  $\text{SiO}_2$ , and which generally comes in very fine particle sizes of less than 1 micron;
- superplasticizer, such as Daracem-100 (W.R. Grace), an expensive but common additive for concrete used to decrease the water requirement for mixing the concrete; and a
- 10 dispersing agent, such as sodium hexametaphosphate ( $\text{Na}_6\text{P}_6\text{O}_{18}$ ). The use of a dispersing agent is particularly preferred when weathered fly ash is incorporated in the hardenable mixture.

- Addition of silica fume can enhance the early rate of strength gain of a hardenable
- 15 mixture, and therefore may be a desirable component of hardenable mixtures of the invention.

- In a specific embodiment, a hardenable mixture of the invention may also contain glass fibers for reinforcement. The use of glass fibers in hardenable mixtures of the invention
- 20 for reinforcement can be achieved because the fly ash, particularly finer fractions of fly ash, reacts more readily than glass fibers with reactive components of the cement, *e.g.*,  $\text{Ca}(\text{OH})_2$ , thus preventing long term reaction of the glass fibers with these reactive components, which would otherwise degrade the glass fibers. The most inert hardenable mixtures are those that contain approximately equal amounts of fly ash, or fly ash and
  - 25 silica fume (as discussed below), and cement. The ability of fly ash to neutralize reactive agents in cement is discussed in greater detail in U.S. Application Serial No. 08/246,861, filed May 20, 1994, and International Patent Publication No. WO 95/32162, published November 30, 1995, of International Application No. PCT/US95/06336, filed May 19, 1995, both entitled "SULFATE AND ACID RESISTANT CONCRETE AND MORTAR"
  - 30 by John Liskowitz et al.

In another specific embodiment, a hardenable mixture of the invention further comprises glass fibers, and silica fume. Silica fume reacts more readily with reactive components of cement than the glass fibers, and thus can provide early desirable protection of the glass

fibers from degradation as well as early compressive strength gains. Subsequently, the fly ash will react with such reactive components, thus precluding early and late reactivity of glass fibers. As noted above, reaction of glass fibers with alkali and alkali earth compounds can lead to degradation of the glass fibers, and loss of tensile strength of the  
5 hardenable mixture.

Concrete beams of the invention with dimensions of 3"x6"x27" can be used to evaluate the bending strength of fly ash concrete, *e.g.*, using simple beam with third-point loading. Preferably, such test procedures are in accordance with ASTM C 78 (1990, ASTM C 78-  
10 84, *Annual Book of ASTM Standards*, Vol 04.02).

The present invention will be better understood by reference to the following Examples, which are provided by way of exemplification and not by way of limitation. The Examples compare various techniques for processing fly ash, including air classification  
15 and grinding, and demonstrate that grinding a specific starting materials under appropriate conditions is necessary to produce a processed fly ash with the advantages disclosed and exemplified herein.

#### EXAMPLE 1: AIR CLASSIFICATION OF FLY ASH

20

Although it has been generally recognized that fly ash produced in utility coal fired boilers when used in small quantities ( $\leq 15\%$ ) as a replacement for cement can provide desirable properties to cement products, its widespread use by the cement industry has been severely limited. This is due to variability in the properties of fly ash collected from  
25 different boilers at different times, its retarding early strength development, and lack of accurate relationship to predict performance of fly ash in cement products when the quantity of the fly ash used as cement replacement exceeds 15%. This occurs because of a lack of understanding of the factors and fly ash properties that influence the performance of the fly ash in combination with the cement in cement products. As a result, fly ash has  
30 been used in small amounts as a generic material in cement to gain improvement in the engineering properties of the cement products without affecting the performance of the cement products that can result from variability in the fly ash properties. The present Examples address these deficiencies, and demonstrates that quantitative utilization of fly ash can be achieved in high quality concrete and mortar compositions.

### Materials and Methods

Twenty super sacs (10 tons total) of marketable fly ash were collected from an electricity generation boiler. An MS-20 commercial air classification fractionator (Progressive Industries, Sylacanga, Alabama) was employed to obtain the desired fly ash product. The  
5 coarse fraction of fly ash that is produced along with the desirable fly ash product in the fractionator was intended to be ground to produce a targeted ground fly ash particle size distribution that is comparable to the fractionated fly ash product.

Grinding of the coarse fraction from the MS-20 Progressive Industry Fractionator was  
10 carried out using a fluidized bed process (Union Processing, Akron, Ohio). As part of this effort, grinding of the fly ash collected from the boiler was also investigated to determine if the desirable fly ash particle sizes in the fly ash could be increased with grinding. Also, dependence of desirable fly ash product on coal pulverizer performance and boiler operating conditions could be minimized through grinding. The amount of fly  
15 ash product with desirable particle sizes available in the fly ash was averaging only about 55 percent of the total particles present in the samples that were collected and analyzed without further processing.

### Results and Discussion

20 Twelve different MS-20 fractionation control settings were evaluated for their effects on product yield. The processing rate was adjusted in the different settings. Increasing the processing rate of the MS-20 from 3 tons/hour up to 5 tons/hr reduced the product yield from 38% down to 28%, respectively. However, particle size analysis using the Leeds and Northrup Microtrac shows that the fly ash product produced at the greater processing  
25 rate of 5 tons/hr (M8F95) contained a greater fraction of fine particle sizes than the product produced at a rate of 3 tons/hour (M9F95). Selecting 11 microns as the desired maximum particle size (diameter) in the product, and 5.5 microns as the mean particle size range for comparison of size distribution, 93% and 78% of the particles in the M8F95 product were less than 11 microns and 5.5 microns, respectively (see Table 1),  
30 whereas 92% and 73% of the particles in the M9F95 are seen to be less than 11 and 5.5 microns (see Table 2). The median particle diameter for the M8F95 and M9F95 fractions was measured to be 2.8 microns and 3.4 microns, respectively.

Table I

MICROTRAC STANDARD RANGE PARTICLE ANALYZER PERCENT PASSING DATA ASVR PARAMETERS		
5	Id #1: M8F95 Distrib. Format: Volume Filter: n/a Run Time: 15 seconds Run Number: Avg of 3 runs Transmission: 0.87 Laser Int: 1.018/0.000/0.000 Residuals: Disabled Above Residual: 0.000 Below Residual: 0.000	Summary Data dv = 0.0579 10% = 1.121 50% = 2.828 90% = 8.924 mv = 4.228 mn = 1.217 ma = 2.306 ca = 2.602 sd = 2.656
10		Chan. Progression: Standard Upper Channel Edge: 704.0 Lower Channel Edge: 0.688 Number of Channels: 20
15		
	<u>Ch Top</u>	<u>% Pass</u>
	704.0	100.00
	497.8	100.00
	352.0	100.00
20	248.9	100.00
	176.0	100.00
	124.5	100.00
	88.00	100.00
	62.23	100.00
25	44.00	100.00
	31.11	99.97
	22.00	99.14
	15.56	96.77
	11.00	92.99
30	7.778	87.54
	5.500	78.41
	3.889	62.95
	2.750	48.82
	1.945	32.16
35	1.375	17.62
	0.972	5.68
		<u>% Change</u>
		0.00
		0.00
		0.00
		0.00
		0.00
		0.00
		0.00
		0.00
		0.03
		0.83
		2.37
		3.78
		5.45
		9.13
		15.46
		14.13
		16.66
		14.54
		11.94
		5.68

Table 2

MICROTRAC STANDARD RANGE PARTICLE ANALYZER PERCENT PASSING DATA ASVR PARAMETERS		
5	Id #1: M9F95 Distrib. Format: Volume Filter: n/a Run Time: 15 seconds Run Number: Avg of 3 runs Transmission: 0.93 Laser Int: 1.016/0.000/0.000 Residuals: Disabled Above Residual: 0.000 Below Residual: 0.000	Summary Data dv = 0.0316 10% = 1.153 50% = 3.357 90% = 10.06 mv = 4.710 mn = 1.220 ma = 2.480 ca = 2.420 sd = 3.130
10		Chan. Progression: Standard Upper Channel Edge: 704.0 Lower Channel Edge: 0.688 Number of Channels: 20
15		
20	<u>Ch Top</u> 704.0 497.8 352.0 248.9 176.0 124.5 88.00 62.23 44.00 31.11 22.00 15.56 11.00 7.778 5.500 3.889 2.750 1.945 1.375 0.972	<u>% Pass</u> 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 99.95 98.84 96.12 91.53 84.49 73.16 55.70 43.03 29.13 16.03 5.19
25		<u>% Change</u> 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.05 1.11 2.72 4.59 7.04 11.33 17.46 12.67 13.90 13.10 10.84 5.19
30		
35		

- 40 A comparison of the compressive strength development exhibited by the M8F95 and M9F95 fly ash-containing mortar in mortar with 25% cement replacement achieved after up to twenty-eight days of curing show differences between the two products. Comparing Figure 1 (M8F95-25) with Figure 2 (M9F95-25), the compressive strength development achieved with the M8F95-25 mortar is seen to be slightly greater than that achieved with
- 45 M9F95-25 mortar up to fourteen days of curing. After twenty eight days of curing, both



the M8F95-25 and M9F95-25 mortar exhibit comparable compressive strength.

Apparently, the finer particle size distribution present in the M8F95 product compared to the M9F95 particle size distribution accounts for faster early compressive strength development exhibited by the M8F95-25 mortar.

5

Mortars were also prepared with M8F95 and M9F95 fly ash products by replacing 35% of the cement with these fly ash products. These mortars did not have observable differences in the rate or extent of compressive strength (compare Figure 3, M8F95-25, with Figure 4, M9F95-35) between them. The use of larger amounts of fly ash in the mortar

10 apparently masks the influence of differences in particle size distribution in the M8F95 and M9F95 products on compressive strength development.

Compressive strength development exhibited by the mortars prepared with 25%

replacement of the cement with the M9F95 fly ash product and the M13N94 fly ash

15 product prepared from ash collected in late 1994 provided comparable results. If one compares Figure 2 with Figure 5, the compressive strengths measured at seven days, fourteen days and twenty eight days of curing can be seen to be comparable for the M9F95-25 and M13N94-25 mortars, respectively.

20 This result was consistent with our predictions from the fineness modulus, since the control setting on the fractionator used to prepare the M13N94 ash provide a processing rate of 3.2 ton/hour which was comparable to the 3 ton/hour processing rate used for the M9F95 product. Particle size analysis indicated their particle size distributions are similar (compare Table 2 with Table 3).

25

Table 3

MICROTRAC STANDARD RANGE PARTICLE ANALYZER PERCENT PASSING DATA ASVR PARAMETERS		
5	Id #1: M13N Distrib. Format: Volume Filter: n/a Run Time: 15 seconds Run Number: Avg of 3 runs Transmission: 0.92 Laser Int: 1.006/0.000/0.000 Residuals: Disabled Above Residual: 0.000 Below Residual: 0.000	Summary Data dv = 0.0392 10% = 1.198 50% = 3.943 90% = 8.718 mv = 4.557 mn = 1.235 ma = 2.638 ca = 2.275 sd = 2.961
10		Chan. Progression: Standard Upper Channel Edge: 704.0 Lower Channel Edge: 0.688 Number of Channels: 20
15		
20	<u>Ch Top</u> 704.0 497.8 352.0 248.9 176.0 124.5 88.00 62.23 44.00 31.11 22.00 15.56 11.00 7.778 5.500 3.889 2.750 1.945 1.375 0.972	<u>% Pass</u> 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00 99.87 98.06 95.54 86.09 69.90 49.29 37.70 25.96 14.27 4.61
25		<u>% Change</u> 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.13 1.81 2.52 9.45 16.19 20.61 11.59 11.74 11.69 9.66 4.61
30		
35		

40 These results indicate that proper settings of the MS-20 fractionator at given feed rates to achieve specific yields of fly ash product can minimize variability in fly ash pozzolanic activity that may exist in fly ash samples collected at different times or from different boilers. Increasing the feed rate increases the quantity of fine particle sizes in the product but at the expense of the product yield.

45

## EXAMPLE 2: GRINDING RESULTS

The coarse fraction (M8CG) produced along with the M8F95 fly ash product in the MS-20 fractionator was selected for grinding. The M8CG fraction was chosen over the M9CG fraction because particle size analysis of these two coarse fractions reveal that 47% of the M8CG fraction particles were below 11 microns and 37% of the M9CG fraction were below 11 microns. Fly ash particle sizes 11 microns and below are the preferred particle sizes for fly ash products to be incorporated in concrete or mortar. Both the grinding of the M8CG coarse fraction and the unfractionated fly ash was investigated using the Union Process Dry Grinding Attritor whose principle of operation is described in Figure 6 (prior art). This grinding process was selected because it was assumed that grinding and rotation of the fly ash particles in an expanded media bed would produce ground particles that are similar in shape to the spherical unground particle. The spherical shape of fly ash particles in cement improves the workability of the fly ash cement product.

A series of six grinding experiments were carried out in a HSA-30 Attritor, which allows scale-up and assessment of the grinding performance of the commercial size Attritor without the need for large quantities of sample. The grinding experiments were carried out by changing the quantity of 2-2.5 mm zirconium silicate beads which served as the grinding media in the Attritor, and the feed rate. The grinding and compressive strength development achieved with the ground M8CG2 product produced from the coarse M8CG fraction and the ground product (M0G95) prepared from the unfractionated fly ash were evaluated.

Microscopic examination of the ground fly ash particles indicates uniformity in shape, comparable to the spherical fractionated fly ash product produced by the air classification process. These results indicate that the Attritor grinding process achieves size reduction by surface grinding as opposed to fracturing the fly ash particles. If fracturing occurred, one would expect to observe irregular shaped particles.

Comparison of the results of the grinding of the M8CG coarse fraction and the unfractionated fly ash shows that the ground products obtained from the unfractionated fly ash (M0G95) is finer than the ground M8CG2 fraction. In this experiment, we found that 90% of the ground M0G95 fly ash product is smaller than 11 microns, and that 73% is

smaller than 5.5 microns, respectively (see Table 4), with the median particle size measured to be 3.0 microns. The percentage of the particle sizes below 11 microns and 5.5 microns measured in the ground M8CG2 product was 89% and 58%, with a median diameter of 4.6 microns (see Table 5).

5

Table 4

10

15

20

MICROTRAC X100 PARTICLE ANALYZER PERCENT PASSING DATA ASVR PARAMETERS		
Id #1: FLY ASH RAW FEED 2 Distrib. Format: Volume Filter: On Run Time: 15 seconds Run Number: Avg of 2 runs Transmission: 0.87 Laser Int: 1.007/0.005/0.999 Residuals: Disabled Above Residual: 0.000 Below Residual: 0.000	Summary Data dv = 0.0518 10% = 0.827 50% = 2.992 90% = 10.75 mv = 21.74 mn = 0.514 ma = 1.820 ca = 3.297 sd = 3.369	Chan. Progression: Standard Upper Channel Edge: 704.0 Lower Channel Edge: 0.122 Number of Channels: 50

	<u>Ch Top</u>	<u>% Pass</u>	<u>% Change</u>
	704.0	100.00	0.00
	592.0	100.00	0.00
	497.8	100.00	0.00
5	418.6	100.00	1.31
	352.0	98.69	2.96
	296.0	95.73	1.32
	248.9	94.41	0.00
	209.3	94.41	0.00
10	176.0	94.41	0.00
	148.0	94.41	0.00
	124.5	94.41	0.00
	104.7	94.41	0.00
	88.00	94.41	0.00
15	74.00	94.41	0.00
	62.23	94.41	0.00
	52.33	94.41	0.00
	44.00	94.41	0.00
	37.00	94.41	0.00
20	31.11	94.41	0.00
	26.16	94.41	0.15
	22.00	94.26	0.45
	18.50	93.81	0.72
	15.56	93.09	1.10
25	13.08	91.99	1.70
	11.00	90.29	2.56
	9.250	87.73	3.71
	7.778	84.02	4.96
	6.541	79.06	6.02
30	5.500	73.04	6.63
	4.625	66.41	6.76
	3.889	59.65	6.51
	3.270	53.14	5.97
	2.750	47.17	5.39
35	2.312	41.78	5.08
	1.945	36.70	5.21
	1.635	31.49	5.71
	1.375	25.78	6.06
	1.156	19.72	5.60
40	0.972	14.12	4.35
	0.818	9.77	3.00
	0.688	6.77	2.03
	0.578	4.74	1.43
	0.486	3.31	1.08
45	0.409	2.23	0.87
	0.344	1.36	0.73
	0.289	0.63	0.63
	0.243	0.00	0.00
	0.204	0.00	0.00
50	0.172	0.00	0.00
	0.145	0.00	0.00

Table 5

5	MICROTRAC X100 PARTICLE ANALYZER PERCENT PASSING DATA ASVR PARAMETERS		
10	Id #1: FLY ASH 8 COARSE Distrib. Format: Volume Filter: On Run Time: 15 seconds Run Number: Avg of 2 runs Transmission: 0.94 Laser Int: 1,007/0.005/0.999 Residuals: Disabled Above Residual: 0.000 Below Residual: 0.000	Summary Data dv = 0.0291 10% = 0.947 50% = 4.577 90% = 11.40 mv = 5.570 mn = 0.479 ma = 2.265 ca = 2.649 sd = 4.093	Time: 10:30 Chan. Progression: Standard Upper Channel Edge: 704.0 Lower Channel Edge: 0.122 Number of Channels: 50
15			

	<u>Ch Top</u>	<u>% Pass</u>	<u>% Change</u>
	704.0	100.00	0.00
	592.0	100.00	0.00
	497.8	100.00	0.00
5	418.6	100.00	0.00
	352.0	100.00	0.00
	296.0	100.00	0.00
	248.9	100.00	0.00
	209.3	100.00	0.00
10	176.0	100.00	0.00
	148.0	100.00	0.00
	124.5	100.00	0.00
	104.7	100.00	0.00
	88.00	100.00	0.00
15	74.00	100.00	0.00
	62.23	100.00	0.00
	52.33	100.00	0.00
	44.00	100.00	0.00
	37.00	100.00	0.00
20	31.11	100.00	0.39
	26.16	99.61	0.66
	22.00	98.95	1.10
	18.50	97.85	1.81
	15.56	96.04	2.81
25	13.08	93.23	4.20
	11.00	89.03	5.88
	9.250	83.15	7.53
	7.778	75.62	8.55
	6.541	67.07	8.64
30	5.500	58.43	7.98
	4.625	50.45	7.02
	3.889	43.43	6.02
	3.270	37.41	5.04
	2.750	32.37	4.20
35	2.312	28.17	3.63
	1.945	24.54	3.44
	1.635	21.10	3.52
	1.375	17.58	3.65
	1.156	13.93	3.46
40	0.972	10.47	2.85
	0.818	7.62	2.10
	0.688	5.52	1.50
	0.578	4.02	1.10
	0.486	2.92	0.87
45	0.409	2.05	0.74
	0.344	1.31	0.68
	0.289	0.63	0.63
	0.243	0.00	0.00
	0.204	0.00	0.00
50	0.172	0.00	0.00
	0.145	0.00	0.00

Differences in particle size distribution between the ground M8CG2 product and the ground  
 55 M0G95 product under the same specific grinding operating conditions using a volume ratio  
 of 2 parts fly ash to one part grinding media appear to be due to the differences in particle  
 size distribution exhibited by the pre-ground M8CG feed and pre-ground fly ash feed. A  
 comparison of particle size distributions show that the particle sizes in the M8CG coarse

ground fly ash feed. A comparison of particle size distributions show that the particle sizes in the M8CG coarse fraction (see Figure 7) is skewed toward the 5 micron to 88 micron range. The unground fly ash contains a broad distribution of sizes, primarily in 0.9 micron to 62 micron range (see Figure 8). The grinding of the two fly ash samples with different particle size distributions resulted in increasing the quantity of particles with sizes below 1.375 and 5.5 microns in the M8CG sample from 6% to 18% and 18% to 58%, respectively, and in the unground fly ash from 14% to 26% and 40% to 73%, respectively.

These data show that direct grinding of the fly ash eliminates the need for initial fractionation of the fly ash followed by grinding of the coarse product to improve the yield. A comparison of the particle size distribution of the M8F95 product produced with the MS-20 fractionation and the M0G95 product achieved with direct grinding of the fly ash suggests that they are similar. The percentage of particle sizes below 11 microns, 5.5 microns, and 1.375 microns in the M8F95 product are 93%, 78%, and 18%, respectively, with a median particle diameter of a 2.8 microns (see Table 1). The percentages for the particle sizes below 11 microns, 5.5 microns, and 1.375 microns in the ground M0G95 product are 90%, 73% and 26%, respectively, with a median diameter of 3 microns (see Table 4).

20

A comparison of the compressive strength development of mortar prepared with 25 percent replacement of cement with the ground M8CG2 and ground M0G95 fly ash shows the ground unfractionated fly ash mortar (M0G95-25) exhibits a faster rate of compressive strength gain, and overall greater compressive strength gain, than the ground coarse fraction (M8CG2-25)-containing mortar up to the twenty eight day design strength. This is observed by comparison of compressive strength development of the M0G95-25 mortar with curing age in Figure 9 with that measured for the M8CG-2-25 mortar in Figure 10. These results are consistent with our expectations based on comparison of the quantity of fine particle sizes in the ground M0G95 product, which is greater than in the ground M8CG2 product.

30

Compressive strength development of mortars, M0G95-25, M0G95-35, M8F95-25, and M8F95-35, prepared with the ground M0G95 unfractionated fly ash product and the fractionated product (M8F95) using 25% and 35% cement replacement with the fly ash



products are comparable. This is seen by comparing the compressive strength development for M8F95-25 mortar in Figure 1 with compressive strength development for M0G95-25 in Figure 9 and compressive strength development M8F95-35 in Figure 3 with that for M0G95-35 in Figure 11.

5

The compressive strength development of the mortars M8F95-25 and M0G95-25, prepared with 25 percent replacement of cement with the fractionated M8F95 product or ground unfractionated M0G95 product, achieves control strength between 7 and 14 days of curing (compare Figure 12 with Figure 1 and Figure 9, respectively). The compressive strength of the M8F95-35 and M0G95-35 mortars prepared with 35 percent placement of cement with the M8F95 and M0G95 fly ash product achieves control strength at 14 days of curing (compare Figure 12 with Figure 3 and Figure 11, respectively).

10

#### Conclusions

Particle surface grinding achieved with the Union Process Attritor provided targeted fly ash particle size distribution and particle shapes that are comparable to the desirable fly ash product produced with the air classification process. Compressive strength development achieved with mortar up to the 28 day design strength using ground unfractionated Mercer fly ash as a cement replacement is comparable to that achieved with the fly ash product produced in the commercial size Progressive Industries MS-20 air classifier. Compressive strength development exhibited by mortar prepared with 25% cement replacement with ground unfractionated fly ash exceeds control compressive strength between 7 and 14 days of curing.

20

Most surprisingly, the grinding process produces a desired fly ash product with 100% product yield without the need for air classification. The use of the grinding process can minimize the dependence of produce yield on operating conditions employed in conventional coal fired utility boilers.

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The fly ash product has been demonstrated to significantly enhance the strength development and durability of concrete. The two major distinct characteristics of the fly ash product are (1) it performs as good as or better than normal cement using the same design mix portions at early age; and (2) it exhibits exceptional resistance against acid and chemical attack. The studies carried out so far utilized conventional mix proportions as

30

recommended by ASTM. No additives or admixtures were added in the tested mix proportions since the studies were aimed at evaluating and understanding the performance characteristics of the fly ash product. These data point the way for developing commercial formulations of fly ash product mortar and concrete for permeability, freeze-thaw resistance, mortar and concrete with early strength, mortar and concrete with strong acid and salt resistance for repair applications, concrete for glass fiber reinforced composites, and concrete with fly ash product and microsilica (silica fume).

10 The present invention is not to be limited in scope by the specific embodiments describe herein. Indeed, various modifications of the invention in addition to those described herein will become apparent to those skilled in the art from the foregoing description and the accompanying figures. Such modifications are intended to fall within the scope of the appended claims.

15

WHAT IS CLAIMED IS:

- 1 1. Fly ash characterized by
  - 2 a) substantially uniform spherical shape;
  - 3 b) greater than about 90% of the particles have a diameter of less than 11
  - 4  $\mu\text{m}$ , greater than about 60% of the particles have a diameter of less than 5.5  $\mu\text{m}$ ,
  - 5 and greater than about 15% of the particles have a diameter of less than 1.375
  - 6  $\mu\text{m}$ ;
  - 7 c) a median particle diameter of less than about 4.0  $\mu\text{m}$ ; and
  - 8 d) a range of particle diameters of from about 0.1  $\mu\text{m}$  to about 70  $\mu\text{m}$ .
- 1 2. The fly ash of claim 1, wherein greater than about 93% of the particles have a
- 2 diameter of less than 11  $\mu\text{m}$ , greater than about 70% of the particles have a diameter of
- 3 less than 5.5  $\mu\text{m}$ , and greater than about 18% of the particles have a diameter of less than
- 4 1.375  $\mu\text{m}$ .
- 1 3. The fly ash of claim 1, wherein the median particle diameter is less than about 3.0
- 2  $\mu\text{m}$ .
- 1 4. The fly ash of claim 1, wherein the range of particle diameters is from about 0.9
- 2  $\mu\text{m}$  to about 62  $\mu\text{m}$ .
- 1 5. The fly ash of claim 1, wherein
  - 2 a) greater than about 93% of the particles have a diameter of less than 11
  - 3  $\mu\text{m}$ , greater than about 70% of the particles have a diameter of less than 5.5  $\mu\text{m}$ ,
  - 4 and greater than about 18% of the particles have a diameter of less than 1.375
  - 5  $\mu\text{m}$ ;
  - 6 b) the median particle diameter is less than about 3.0  $\mu\text{m}$ ; and
  - 7 c) the range of particle diameters is from about 0.9  $\mu\text{m}$  to about 62  $\mu\text{m}$ .
- 1 6. The fly ash of claim 5, which is prepared by grinding unfractionated fly ash.
- 1 7. A concrete comprising about 1 part by weight cementitious materials, about 1 to
- 2 about 3 parts by weight fine aggregate, about 1 to about 5 parts by weight coarse

3 aggregate, and about 0.35 to about 0.6 parts by weight water, wherein the cementitious  
4 materials comprise from about 10% to about 50% by weight the fly ash of claim 1 and  
5 about 50% to about 90% by weight cement.

1 8. A concrete comprising about 1 part by weight cementitious materials, about 1 to  
2 about 3 parts by weight fine aggregate, about 1 to about 5 parts by weight coarse  
3 aggregate, and about 0.35 to about 0.6 parts by weight water, wherein the cementitious  
4 materials comprise from about 10% to about 50% by weight the fly ash of claim 5 and  
5 about 50% to about 90% by weight cement.

1 9. The concrete of claim 7 further comprising silica fume.

1 10. The concrete of claim 7 further comprising glass fibers.

1 11. A mortar comprising about 1 part by weight cementitious materials, about 1 to  
2 about 3 parts by weight fine aggregate, and about 0.35 to about 0.6 parts by weight water,  
3 wherein the cementitious materials comprise from about 10% to about 50% by weight the  
4 fly ash of claim 1 and about 50% to about 90% by weight cement.

1 12. A mortar comprising about 1 part by weight cementitious materials, about 1 to  
2 about 3 parts by weight fine aggregate, and about 0.35 to about 0.6 parts by weight water,  
3 wherein the cementitious materials comprise from about 10% to about 50% by weight the  
4 fly ash of claim 5 and about 50% to about 90% by weight cement.

1 13. The mortar of claim 12 further comprising silica fume.

1 14. The mortar of claim 12 further comprising glass fibers.

1 15. Fly ash prepared by processing fly ash so as to shift the size distribution to have  
2 the following characteristics:

- 3 a) substantially uniform spherical shape;  
4 b) greater than about 90% of the particles have a diameter of less than 11  
5  $\mu\text{m}$ , greater than about 60% of the particles have a diameter of less than 5.5  $\mu\text{m}$ ,  
6 and greater than about 15% of the particles have a diameter of less than 1.375

7             $\mu\text{m}$ ;

8            c)        a median particle diameter of less than about 4.0  $\mu\text{m}$ ; and

9            d)        a range of particle diameters of from about 0.1  $\mu\text{m}$  to about 70  $\mu\text{m}$ .

1    16.     The fly ash of claim 15 wherein the processing comprises grinding with a fluid  
2    bed grinding process using a ratio of two parts unfractionated fly ash with one part  
3    grinding media (by volume).

1    17.     The fly ash of claim 16 wherein the grinding media is zirconium silicate.

1    18.     The fly ash of claim 16 wherein the grinding media is carbon steel.

1    19.     A concrete comprising about 1 part by weight cementitious materials, about 1 to  
2    about 3 parts by weight fine aggregate, about 1 to about 5 parts by weight coarse  
3    aggregate, and about 0.35 to about 0.6 parts by weight water, wherein the cementitious  
4    materials comprise from about 10% to about 50% by weight the fly ash of claim 15 and  
5    about 50% to about 90% by weight cement.

1    20.     A concrete comprising about 1 part by weight cementitious materials, about 1 to  
2    about 3 parts by weight fine aggregate, about 1 to about 5 parts by weight coarse  
3    aggregate, and about 0.35 to about 0.6 parts by weight water, wherein the cementitious  
4    materials comprise from about 10% to about 50% by weight the fly ash of claim 17 and  
5    about 50% to about 90% by weight cement.

1    21.     The concrete of claim 19 further comprising silica fume.

1    22.     The concrete of claim 19 further comprising glass fibers.

1    23.     A mortar comprising about 1 part by weight cementitious materials, about 1 to  
2    about 3 parts by weight fine aggregate, and about 0.35 to about 0.6 parts by weight water,  
3    wherein the cementitious materials comprise from about 10% to about 50% by weight the  
4    fly ash of claim 15 and about 50% to about 90% by weight cement.

1    24.     A mortar comprising about 1 part by weight cementitious materials, about 1 to

- 2 about 3 parts by weight fine aggregate, and about 0.35 to about 0.6 parts by weight water.  
3 wherein the cementitious materials comprise from about 10% to about 50% by weight the  
4 fly ash of claim 17 and about 50% to about 90% by weight cement.

1 25. The mortar of claim 23 further comprising silica fume.

1 26. The mortar of claim 23 further comprising glass fibers.

1 27. A method for preparing fly ash comprising processing fly ash so as to shift the  
2 size distribution to have the following characteristics:

- 3 a) substantially uniform spherical shape;  
4 b) greater than about 90% of the particles have a diameter of less than 11  
5  $\mu\text{m}$ , greater than about 60% of the particles have a diameter of less than 5.5  $\mu\text{m}$ ,  
6 and greater than about 15% of the particles have a diameter of less than 1.375  
7  $\mu\text{m}$ ;  
8 c) a median particle diameter of less than about 4.0  $\mu\text{m}$ ; and  
9 d) a range of particle diameters of from about 0.1  $\mu\text{m}$  to about 70  $\mu\text{m}$ .

1 28. The method according to claim 27 wherein the processing comprises grinding with  
2 a fluid bed grinding process using a ratio of two parts unfractionated fly ash with one part  
3 grinding media (by volume).

1 29. The method according to claim 28 wherein the grinding media is zirconium  
2 silicate.

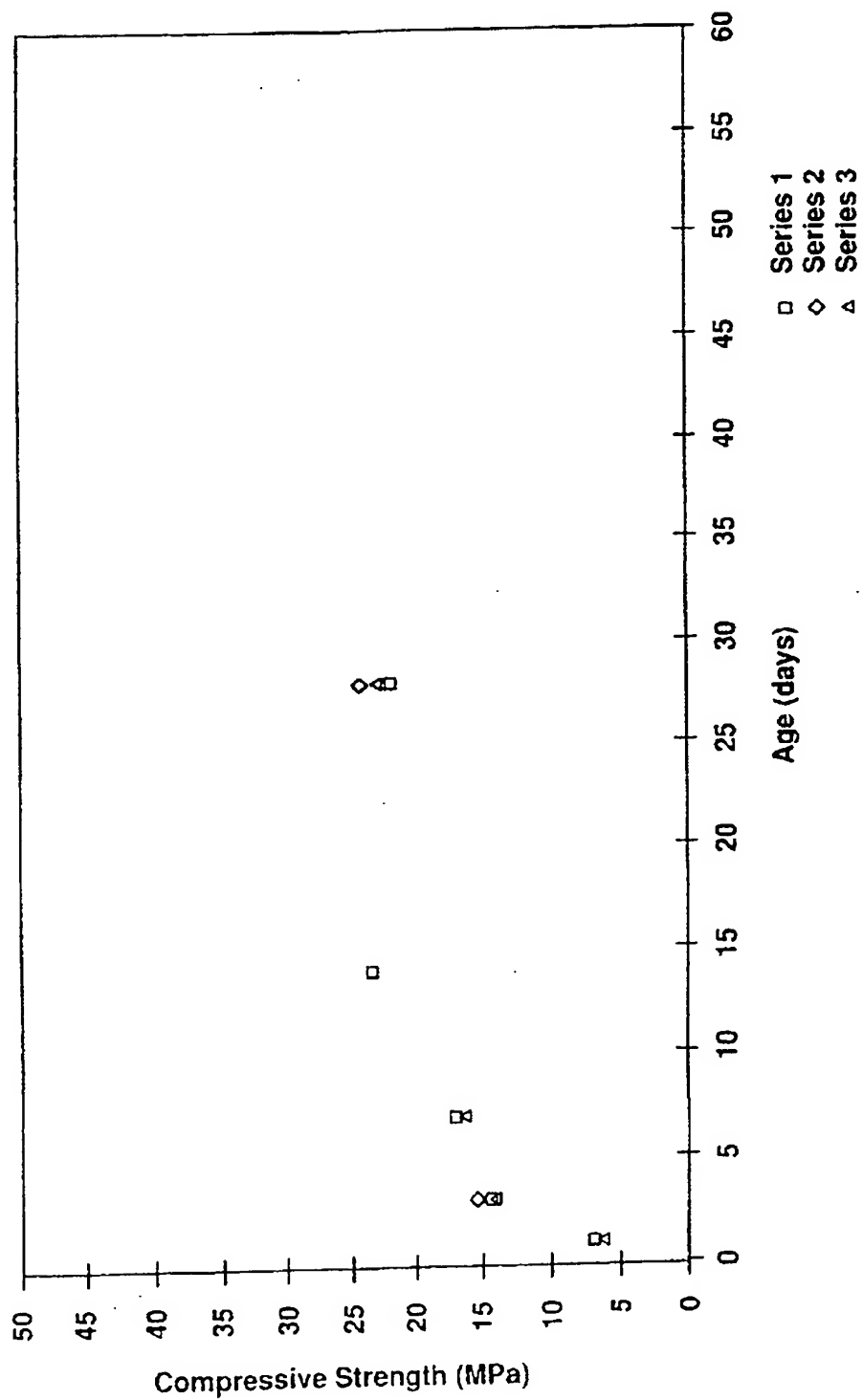
1 30. The method according to claim 28 wherein the grinding media is carbon steel.

1 31. The method according to claim 27 wherein the fly ash is dry bottom boiler fly  
2 ash.

1 32. The method according to claim 27 wherein the fly ash is wet bottom boiler fly  
2 ash.

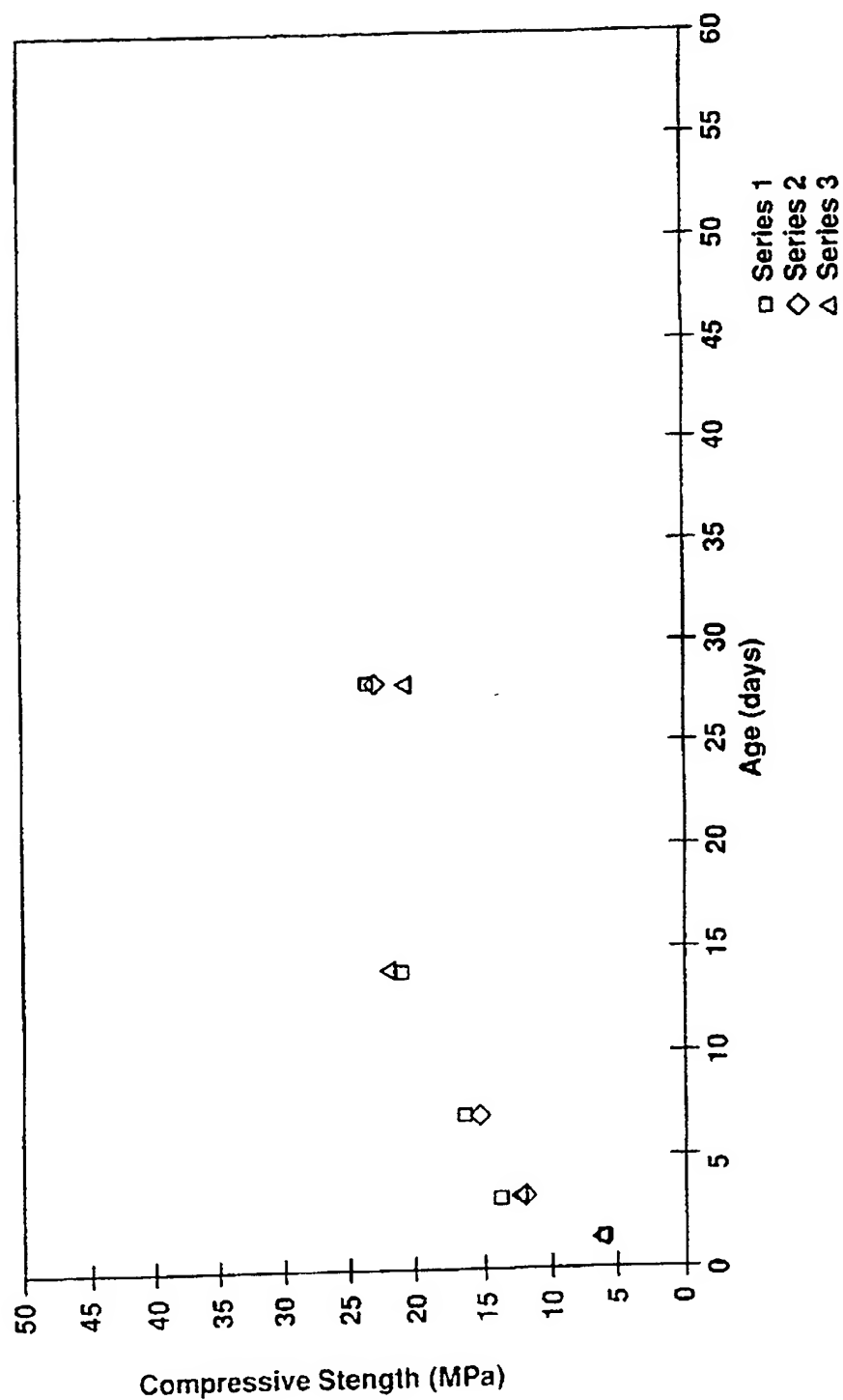
1 / 13

FIG. 1



2 / 1 3

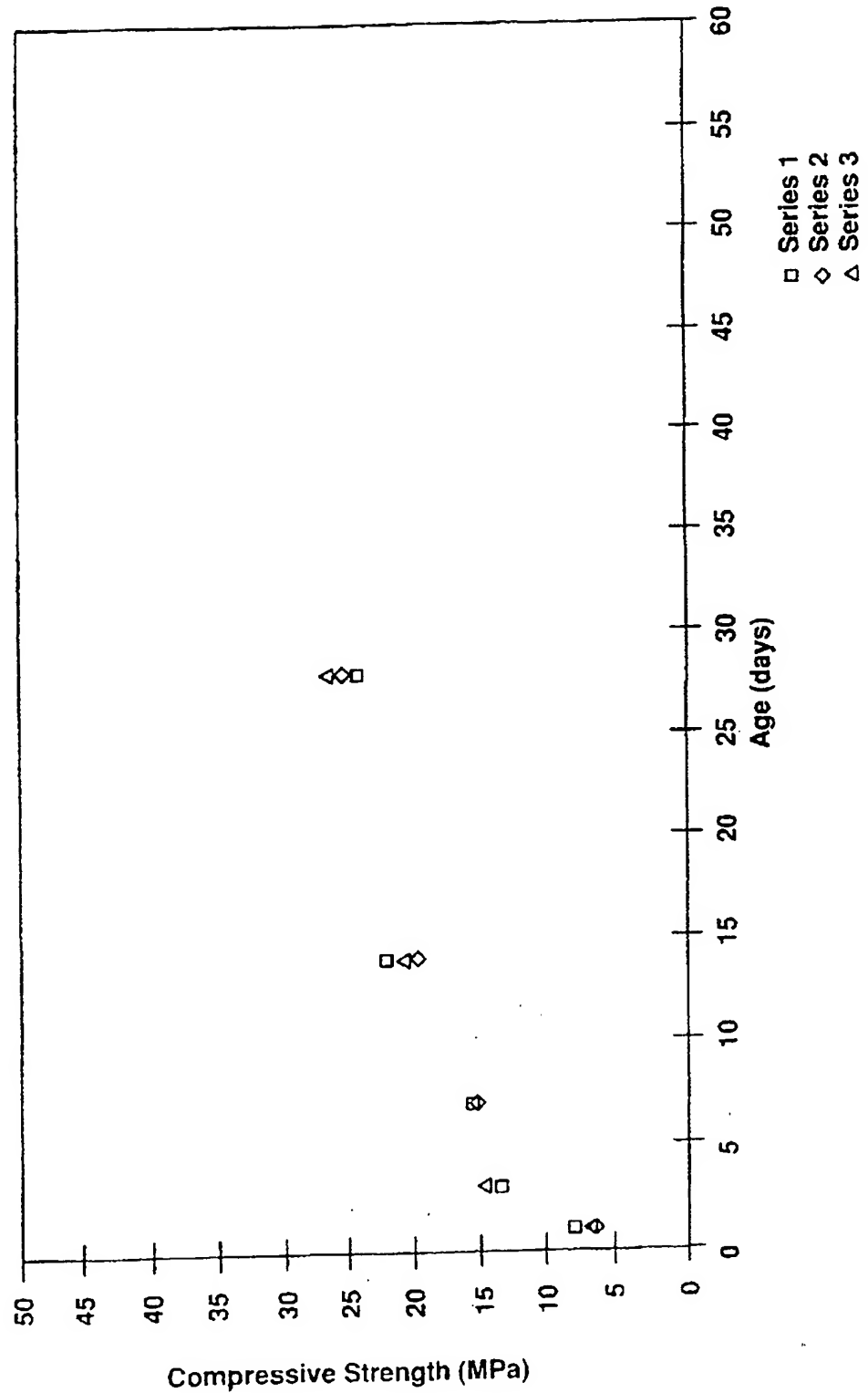
FIG.2





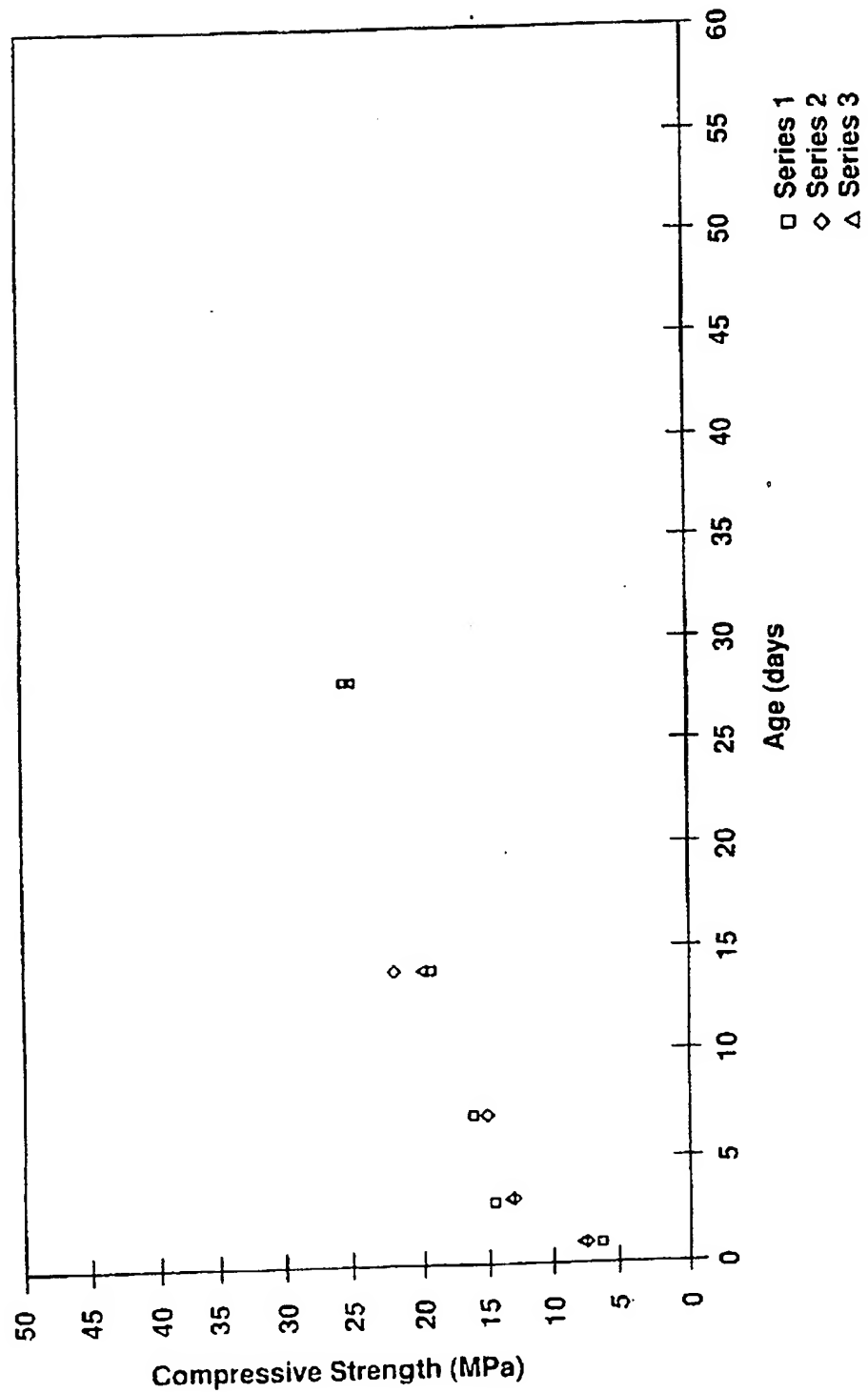
3 / 1 3

FIG.3



4 / 13

FIG.4



5 / 13

FIG.5

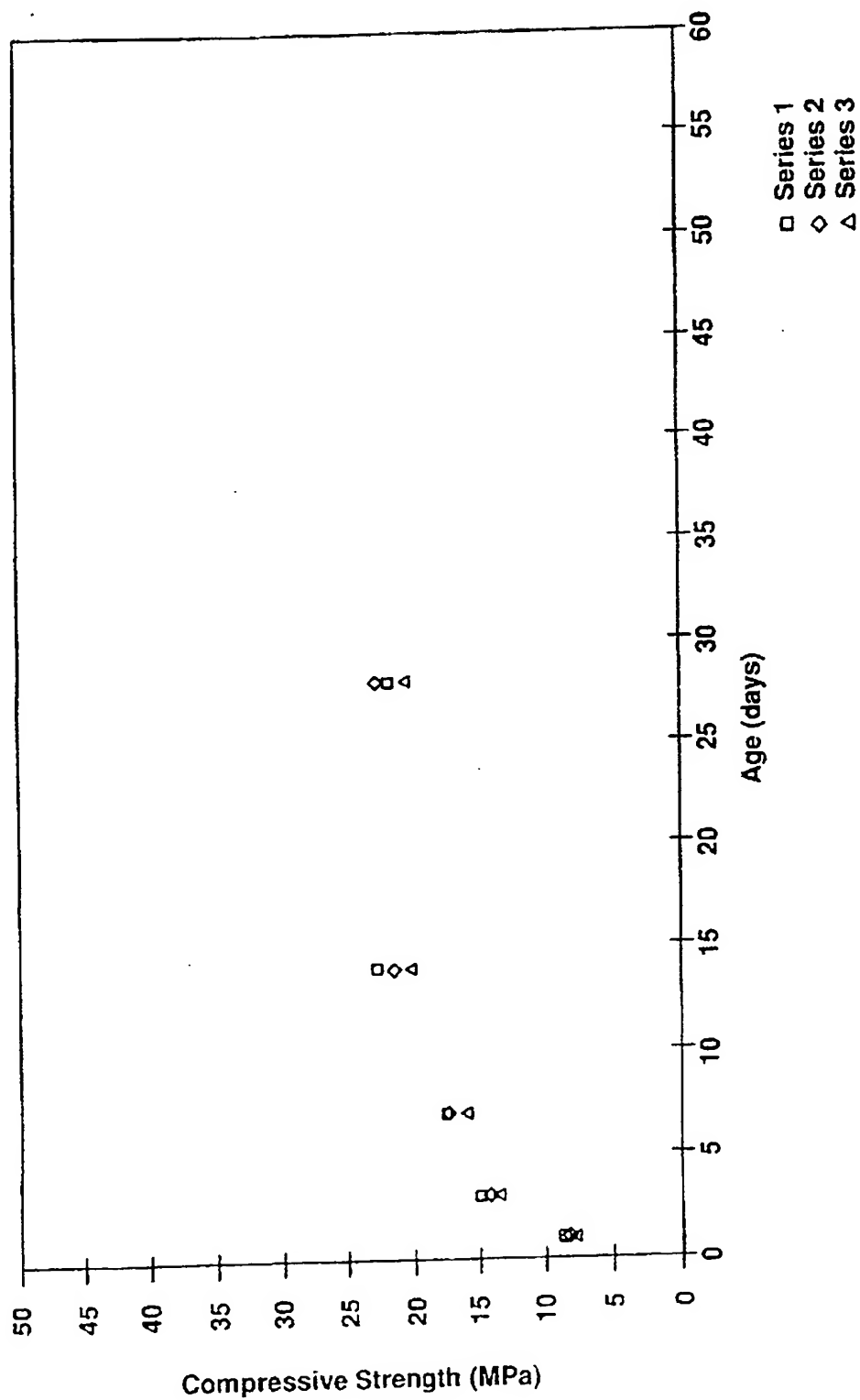
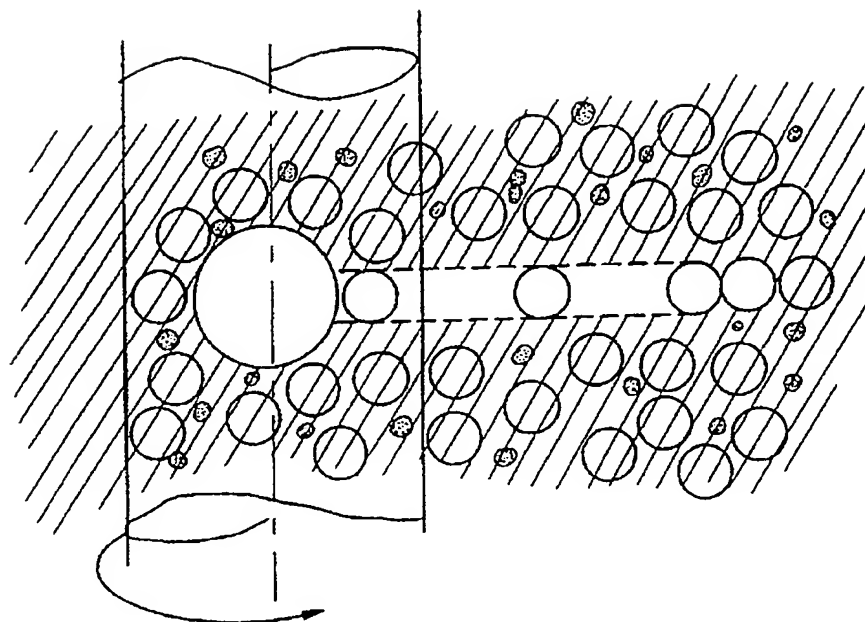


FIG.6A



Revolving arm hits  
grinding media

Media moves  
forward rapidly

Media collides with  
media, breaking up  
product particle

7 / 13

FIG.6B

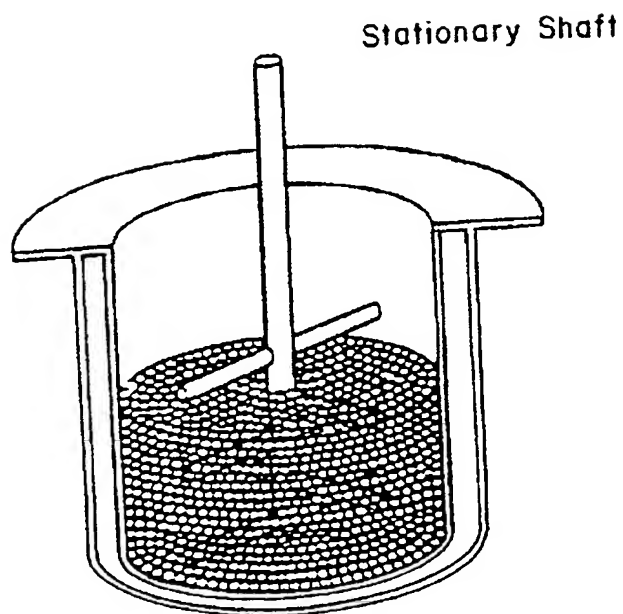
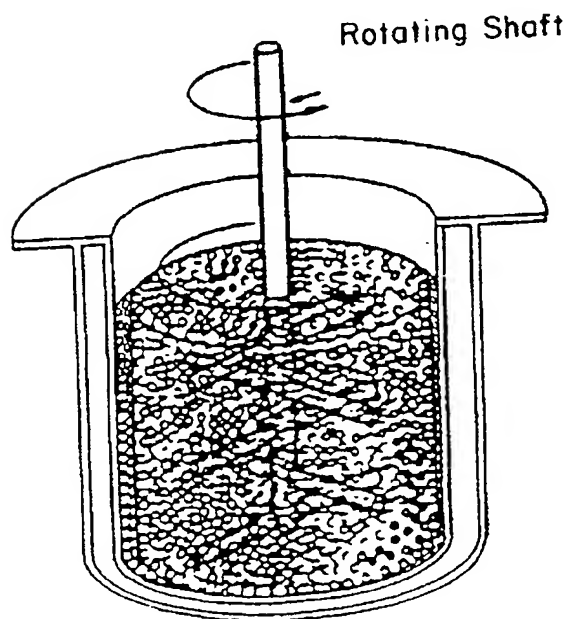
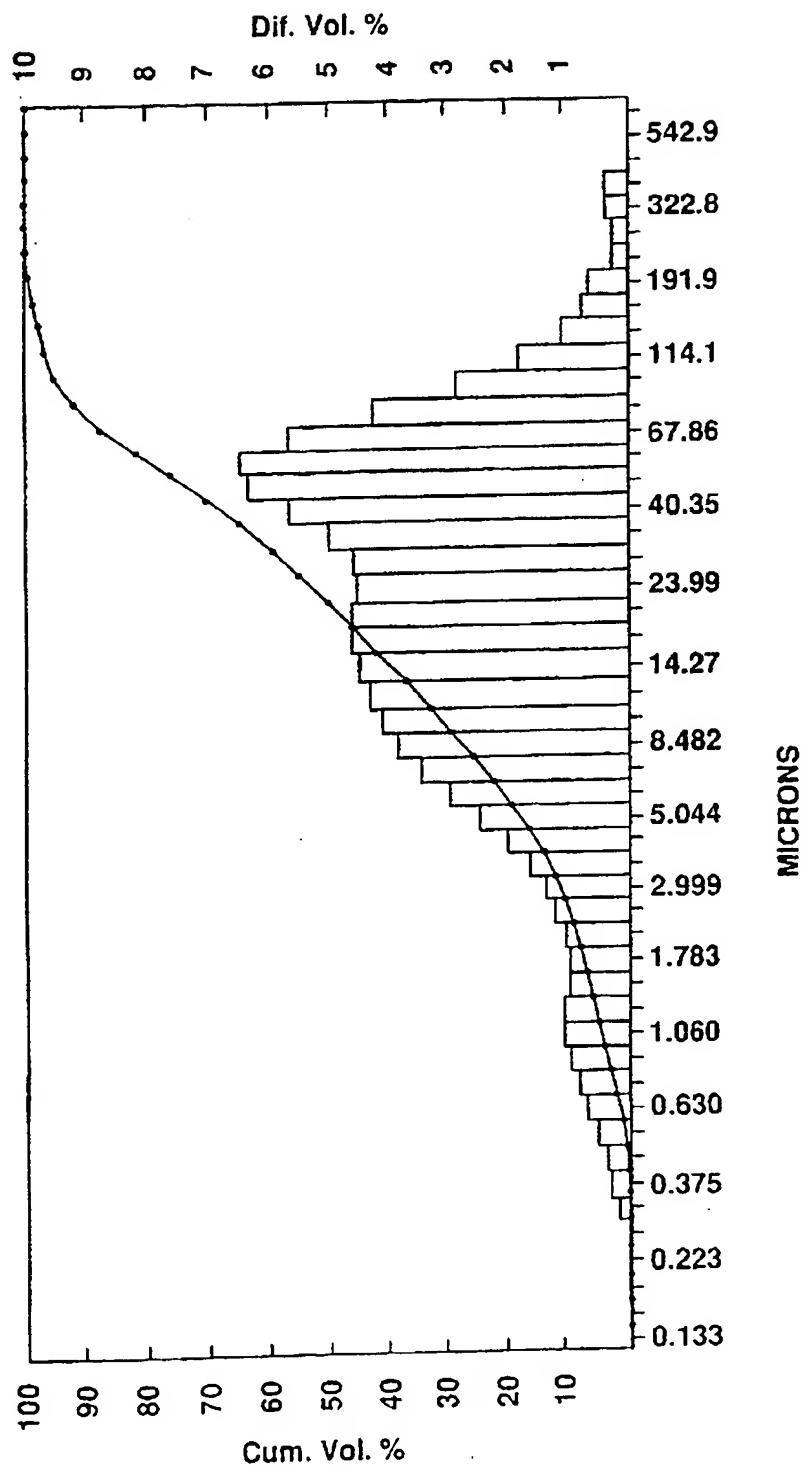


FIG.6C



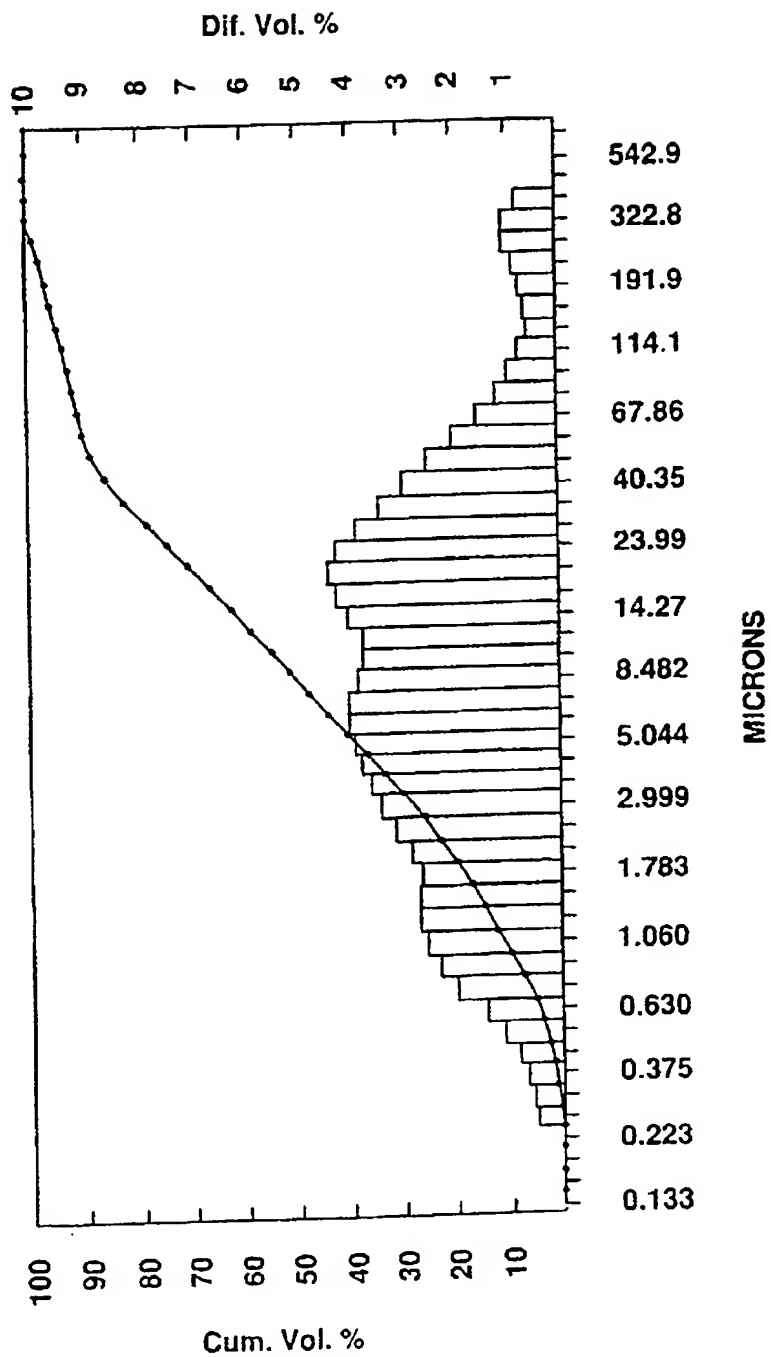
8 / 13

FIG. 7



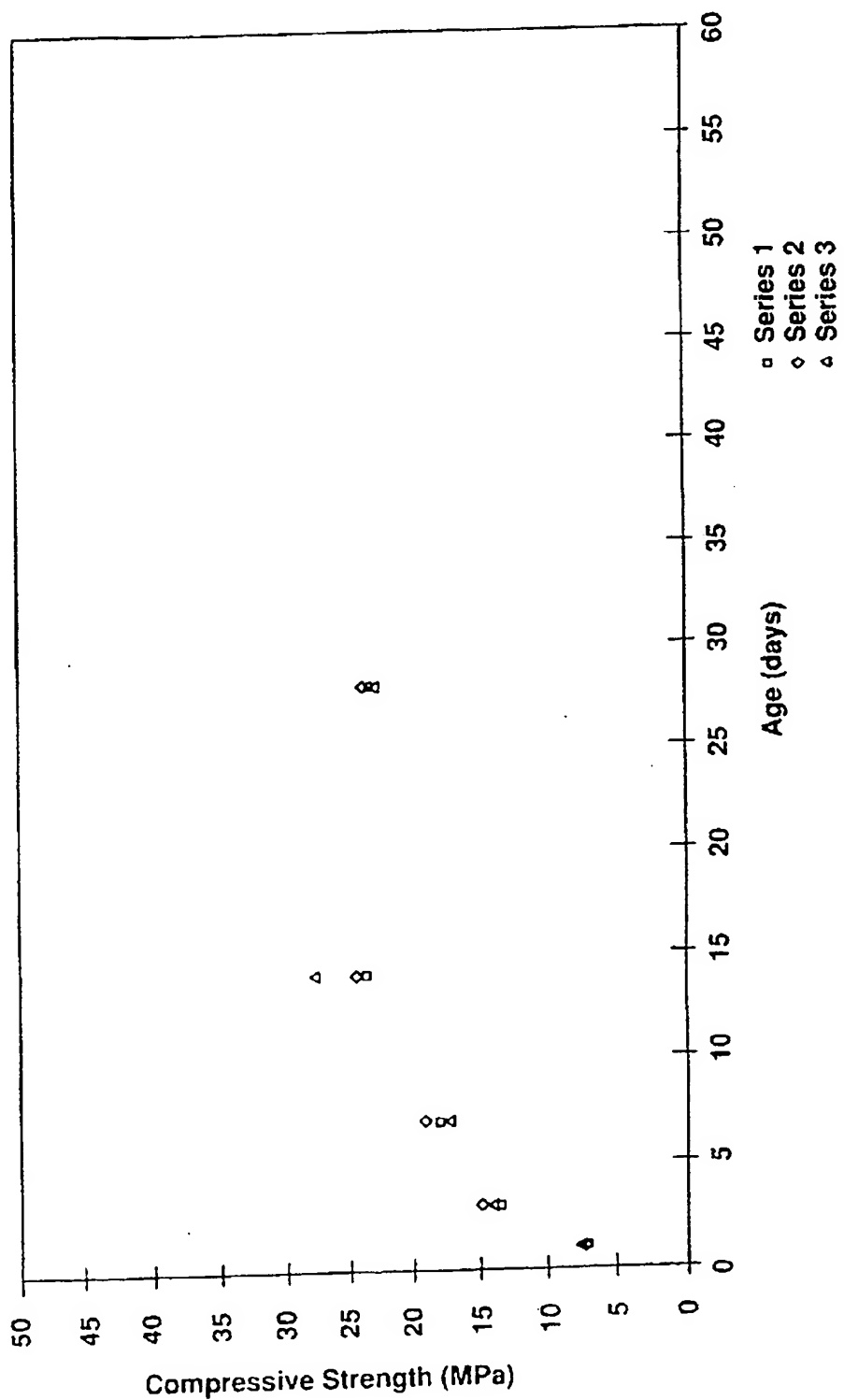
9 / 13

FIG.8



10 / 13

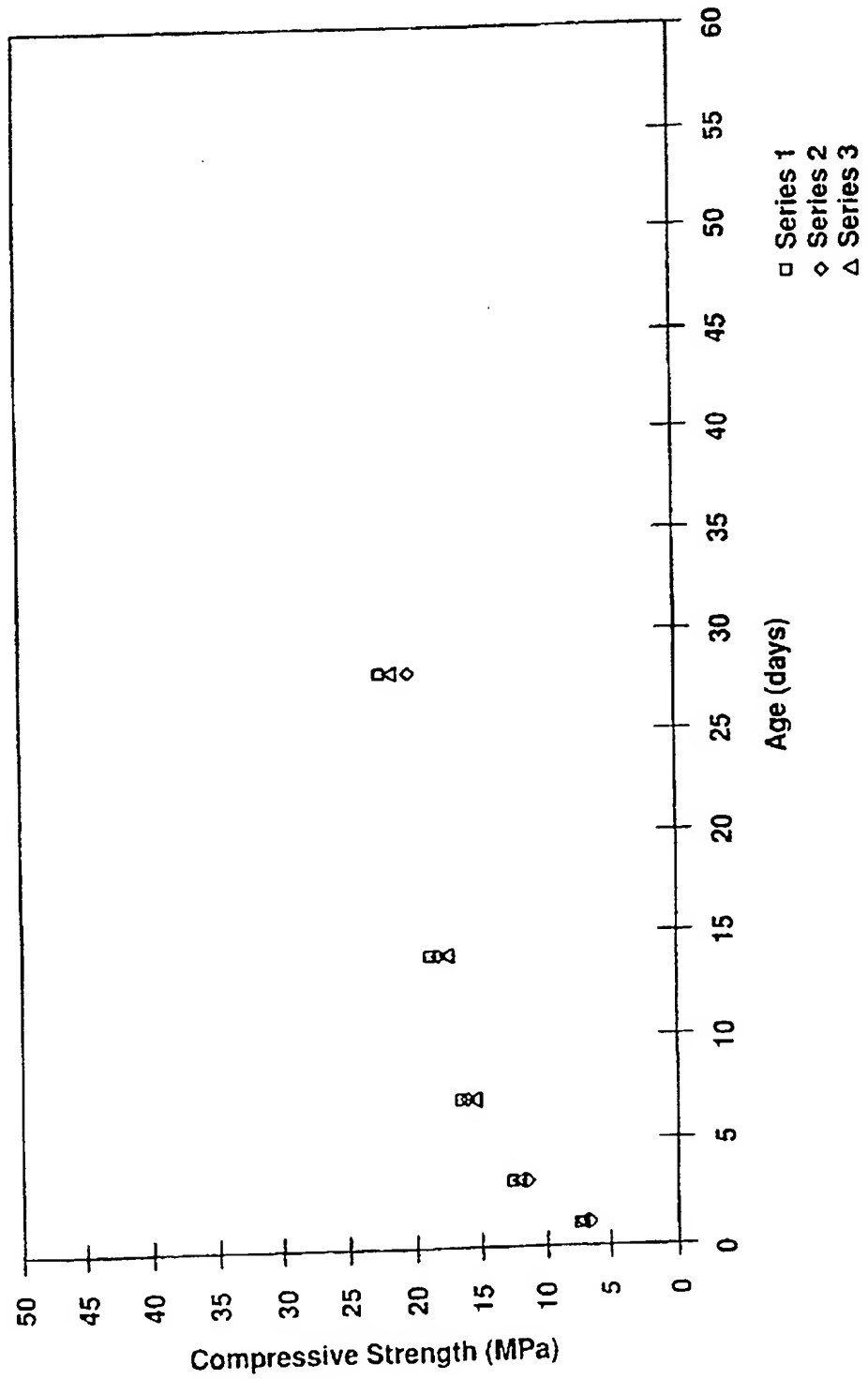
FIG. 9





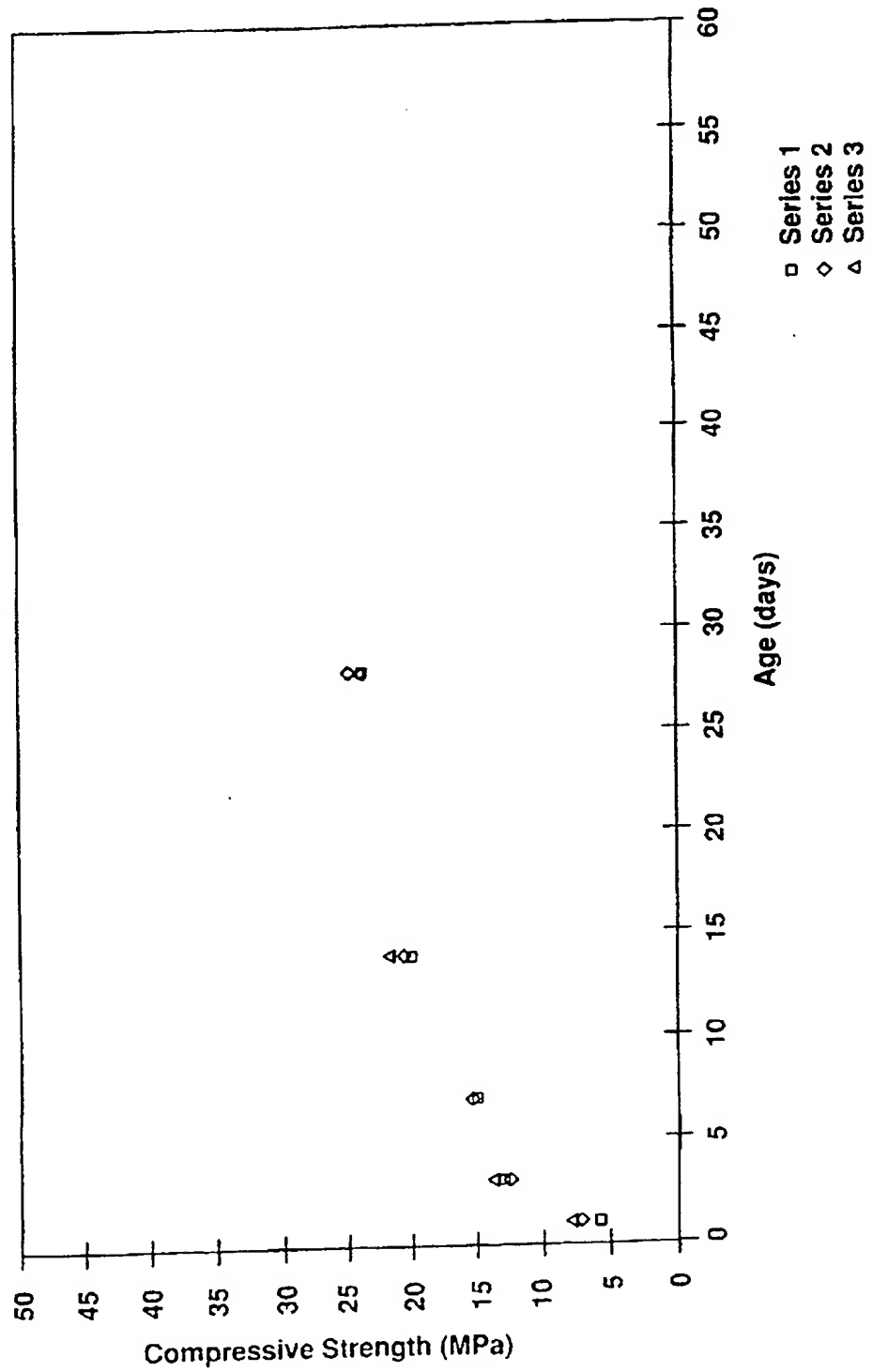
11 / 13

FIG.10



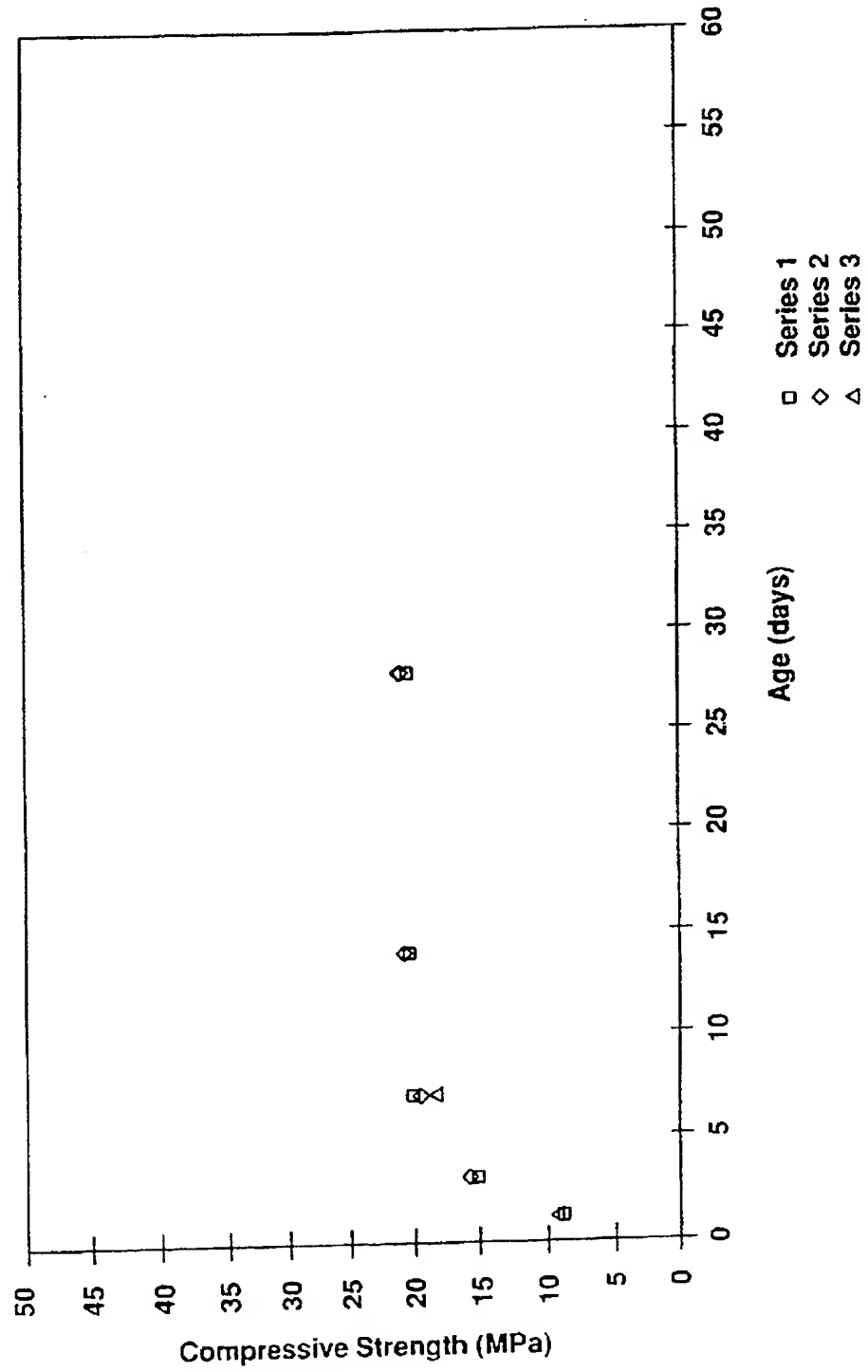
12 / 13

FIG. 11



13 / 13

FIG.12



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/19936

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C04B 14/00, 14/02, 14/04, 14/36, 18/04  
US CL :106/405, 705, 709, 711, 737, 819, DIG 1; 264/DIG49  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/405, 705, 709, 711, 737, 819, DIG 1; 264/DIG49  
IPC(6):14/00, 14/02, 14/04, 14/36, 18/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
None

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2,250,107 A (NELLES) 22 JULY 1941, SEE COLUMN 2, LINE 43-COLUMN 10, LINE 40.	1-32
Y	US 4,210,457 A (DODSON ET AL.) 01 JULY 1980, SEE COLUMN 2, LINES 22-43 AND COLUMN 7, LINES 4-21.	1-32
Y	US 2,987,408 A (MINNICK) 06 JUNE 1961, SEE COLUMN 2, LINE 65-COLUMN 4, LINE 20.	1-32
A	US 3,669,703 A (PENNACHETTI) 13 JUNE 1972, SEE COLUMN 2, LINE 48-COLUMN 3, LINE 15 AND THE EXAMPLES.	1-6, 15-18, 27-32

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be of particular relevance
* E		earlier document published on or after the international filing date
* L		documents which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* O		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	documents of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	documents of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* A	document member of the same patent family

Date of the actual completion of the international search

11 FEBRUARY 1997

Date of mailing of the international search report

04 APR 1997

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/19936

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	UKITA ET AL., "IMPROVEMENTS IN THE PROPERTIES OF CONCRETE UTILIZING "CLASSIFIED FLY ASH", "FLY ASH, SILICA FUME, SLAG, AND NATURAL POZZOLANS IN CONCRETE", THIRD INTERNATIONAL CONFERENCE TRONDHEIM, NORWAY, 1989, VOLUME 1, PAGES 221, 227 AND 233.	1-32
Y	US 4,504,320 A (RIZER ET AL.), 12 MARCH 1985, SEE COLUMN 2, LINE 30-COLUMN 3, LINE 51 AND THE CLAIMS.	10,14,22, 26